Parts of the work contained in this thesis have been published in the scientific literature, with the following references:-

P.N.Hawker, L.S.Jenkins and G.R.Willey. J. Organometallic Chem. 118 C44 (1976)

L.S.Jenkins and G.R.Willey. Inorg. Chim. Acta. 29 L201 (1978)

S.O.Wandiga, L.S.Jenkins and G.R.Willey. J. Inorg. Nuclear Chem. 41 941 (1979)

L.S.Jenkins and G.R.Willey. J. Chem. Soc. Dalton. 777 (1979)

L.S.Jenkins and G.R.Willey. J. Chem. Soc. Dalton. 1697 (1979)

COORDINATION CHEMISTRY OF TRANSITION METAL HALIDES AND CARBONYL COMPOUNDS.

BY

LINDA S. JENKINS.

A dissertation submitted, in part fulfilment of the requirements for the degree of Doctor of Philosphy, to the department of Chemistry and Molecular Sciences, Warwick University.

April 1980.

ABSTRACT.

The coordination chemistry of various transition metal halides and carbonyl compounds has been investigated from several viewpoints.

The coordination behaviour of 1,3,2,4 diazadiphosphetidines, exemplified by $(ClPNBu^t)_2$, towards metal halides and carbonyls has been studied. Novel metal complexes incorporating the four-membered ring system as a bidentate P-donor have been characterized. Both bridging and chelating behaviour was observed.

From the reactions of $Fe_2(CO)_9$ with the potentially tetradentate N-donors, TREN, Me_6TREN and TRIEN, both mono-and bi-nuclear complexes have been isolated. However in all cases the ligand appeared to be denyed a tetradentate mode of attachment.

For the MCl_3/NMe_3(M=Ti,V and Cr) systems, a second, mono-adduct was identified for each case, namely $[MCl_2(NMe_3)]$ (M=Ti,Cr) and $[VCl_3(NMe_3)]$.

The reactions of $(C_5H_5)_2Ti(SEt)_2$ with $[MCl_3(THF)_3]$ (M=Ti, V and Cr) have been studied in a preliminary investigation into possible routes to mixed-valence compounds. From the evidence collected we find that ligand exchange occurs rather than formation of the desired mixed-valence species.

As a result of collaboration with Nairobi University, the reactions of thiourea with the group VB trihalides have been investigated. Spectral data provided evidence for coordination of thiourea via the sulphur atom in all complexes except the PCl_3 case, for which unambiguous characterization was not achieved. A further study of the antimony complexes as possible schistosomicides is being carried out at Nairobi University.

CONTENTS

LIST OF TABLES.

LIST OF FIGURES.

ACKNOWLEDGEMENTS.

I would like to thank Dr.G.R. Willey for all his help and encouragement throughout the period of this work. I would also like to thank the technicians and staff of the Department of Chemistry and Molecular Sciences who have assisted me in numerous ways during my stay at Warwick.

Especial thanks to my mother, for help in the typing of this thesis, and my father and Martin for their support and encouragement in times of doubt.

The award of a research studentship from the Science Research Council is gratefully acknowledged.

ABBREVIATIONS.

Me	=	Methyl
Et	=	Ethyl
Bu^n	=	n-Butyl
Bu^t	=	t-Butyl
Ph	=	Phenyl
py	=	Pyridine
bipy	=	Bipyridine
THF	=	Tetrahydrofuran
TREN	=	Tris(2-aminoethyl)amine
Me_6TREN	=	Tris(2-dimethylaminoethyl)amine
TRIEN	=	1,4,7,10 tetrazadecane
tu	=	Thiourea
DMF	=	Dimethylformamide

Used in experimental details:

w	=	weak
m	=	medium
s	=	strong
v	=	very
br	=	broad
sh	=	shoulder

CHAPTER ONE.

INTRODUCTION.

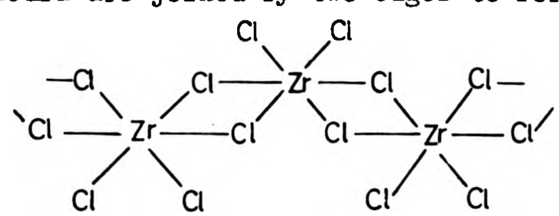
1A COORDINATION CHEMISTRY.

In this research project several different systems were studied in the general area of inorganic coordination chemistry. The overall view was to investigate the coordination behaviour of a variety of donors towards selected metals by synthesis and characterization of their complexes. As a consequence of the diversity of systems studied a detailed review of each seems inappropiate here. Rather, a broader discussion of the more fundamental aspects that make up a classical coordination study is deemed more pertinent. In addition, each chapter will have a short introduction of its own giving the relevant background.

Coordination Compounds.

The term "coordination compound" is extremely difficult to define. Historically it was used to describe compounds in which the number of ligands exceeded the oxidation number of the central atom. Such compounds offered an intriguing challenge to the early inorganic chemist since they appeared to defy the usual rules of valence. Nowadays the term is used to embrace all species, charged or uncharged, in which a central atom is surrounded by a set of atoms or molecules, termed ligands. (See also Appendix B).
The ligands need not be small independent atoms molecules, but may involve fairly elaborate molecules attached by more than one coordinating atom, that is chelating ligands.
Many metal ions not only exhibit more than one coordination number for any given oxidation state, but also more than

one geometrical configuration for the same coordination number. For example nickel (II) may adopt six-coordinate octahedral, five-coordinate square pyramidal, four-coordinate tetrahedral and four-coordinate square planar structures depending on the nature of the ligands. Coordination numbers cannot, necessarily, be determined on the basis of elemental composition alone. Molecules may combine through bridging ligands atoms or directly via metal - metal bonds so that, although titanium (IV) chloride is monomeric and tetrahedral [1] crystalline zirconium (IV) chloride has a polymeric chain structure in which $ZrCl_6$ octahedra are joined by two edges to form a zig-zag chain (A).[2]



A

1B STRUCTURAL CONSIDERATIONS.

When studying coordination compounds it is necessary to be aware of the possible geometrical configurations which may be adopted for each coordination number. For "typical" coordination compounds, coordination numbers from two to nine are usual, although examples of higher coordination numbers are known.

Coordination Number Two

Few complexes are known with coordination number two, and they are generally limited to the 1+ ions of the group IB metals and the closely related Hg (II) species. Of the two geometric possibilities, linear or bent, the former predominates in these heavy metal complexes; example include $[Au(PPh_3)_2]^+I^-$ [3] and $Pd(PPhBu^t{}_2)_2$[4,5]. Bulky ligands can often force metal atoms to adopt low coordination numbers, for example $(Me_3Si)_2N$-. The cobalt (II) complex of this ligand exhibited molecular weight values, electronic spectra and other physical properties consistent with a monomeric formulation, $Co[N(SiMe_3)_2]_2$ in which the cobalt has the unusual coordination number two.[6]

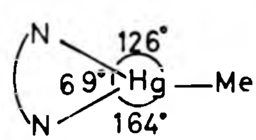
Coordination Number Three

Three coordinate complexes have only recently been examined in any detail, but the range now known is fairly wide.[7] The great majority involved the bulky bis(trimethylsilyl)-amido group, mentioned above, bound to a variety of metal centres. These complexes, $M[N(SiMe_3)_2]_3$, fall into two structural types:-

i) Trigonal planar MN_3 configuration [8,9] (Fig. 1.1) examples of which include M= Ti, V, Cr, Fe, Al, Ga and In.

ii) pyramidal MN_3 configuration [10] (Fig. 1.2), where M=Sc, Eu and Yb.

The configurations of three-coordinate complexes are not restricted to perfect trigonal planar and trigonal pyramidal structures. Deviations from perfect symmetry do occur, for example the $[Hg(Me)(bipy)]^{2+}$ cation is markedly distorted from trigonal symmetry (B). [11]



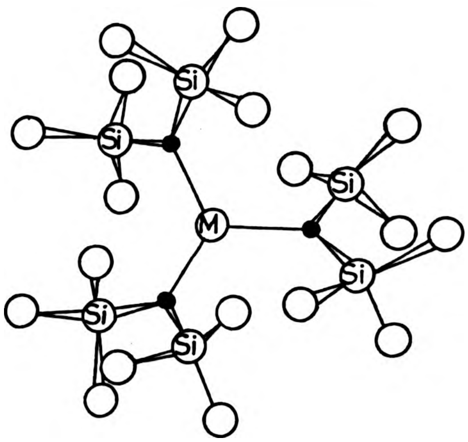


Fig. 1.1. Crystal and Molecular Structure of Tris (hexamethyldisilylamido) iron (III)

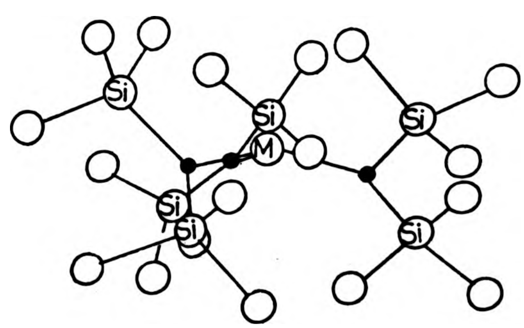


Fig. 1.2. Crystal and Molecular Structure of Tris (hexamethyldisilylamido) scandium (III)

Coordination Number Four.

With coordination number four the structures adopted may be conveniently divided into tetrahedral and square planar forms, although intermediate and distorted structures are known.

Tetrahedral complexes are favoured by sterically bulky ligands and small metal ions of three types:

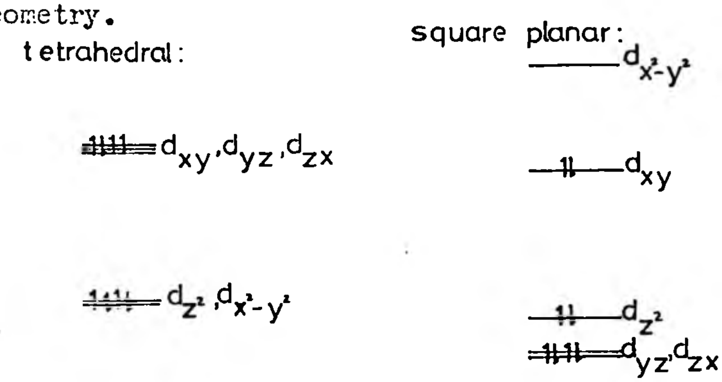
a) those with a noble gas configuration eg. Be(II)

b) those with a pseudo-noble gas configuration eg. Zn(II)

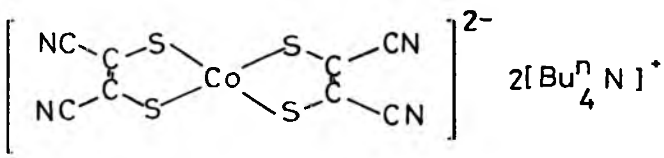
c) those transition-metal ions which do not strongly favour other structures, such as Co(II).

There are innumerable examples of tetrahedral and distorted tetrahedral complexes. For example many copper (I) complexes are tetrahedral such as the $[Cu(CN)_4]^{3-}$ ion in $K_3Cu(CN)_4$ [12] and $[Cu(PPh_3)_2(NO_3)]$.[13]

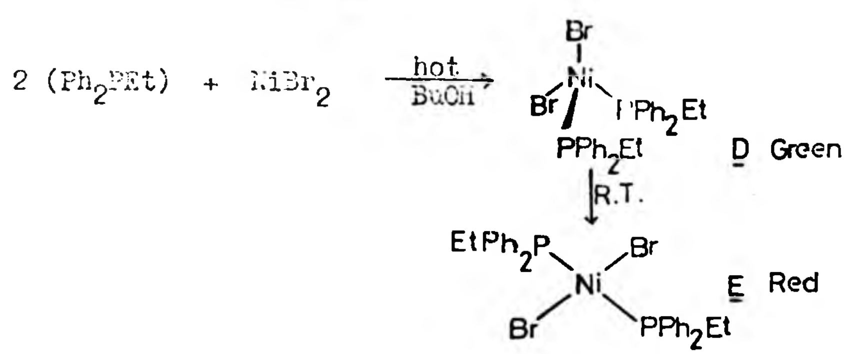
Square planar complexes are less favoured sterically and may be crowded by large ligands. With small ligands, formation of an octahedral complex with two additional σ-bonds can occur with little or no additional steric repulsion. Consequently square-planar complexes are formed with only a few metal ions, the majority of which have a d^8 electronic configuration, ie. Rh(I), Ir(I), Ni(II), Pd(II), Pt(II) and Au(III). An explanation for this can be seen by inspection of the splitting of the d-orbitals when placed in the different crystal fields. For d^8, in the square planar configuration, the highest energy level is left unoccupied and this configuration is stabilized relative to a tetrahedral geometry.



Other metals may also form square planar complexes with appropriate ligands, such as 1, 2 dithiolates,[14,15] eg. the bis(maleonitrile dithiolato) cobalt (II) anion,[16] (C).



Four-coordinate complexes may exist in both tetrahedral and square planar configurations depending on conditions. For example addition of ethyldiphenylphosphine to nickel (II)-bromide gives green, tetrahedral $[(Ph_2PEt)_2NiBr_2]$ (D), which gives a red solution in benzene or carbon disulphide. On cooling the red solution to 195K, dark red crystals of the square-planar isomer (E) are obtained:-[17,18]



Coordination Number Five.

One of the most active areas of research in structural chemistry in recent years has concerned five coordination, examples are known for all the first-row transition metals from titanium to zinc.[19-22] Steric rather than electronic factors generally influence the formation of five-coordinate complexes. A large number of such complexes have been prepared by using sufficiently bulky ligands so that non-bonding repulsions limit the coordinations number to five. Others by the design of multidentate ligands in which the interdoncr atom distances and angles closely match the edges of the coordination polyhedra. Probably the best known of this latter group are the tripod ligands, $(AX)_3B$, where A and B are donor atoms and X is an organic residue. Such ligands have three-fold symmetry which they can impose upon the metal ion to produce trigonal bipyramidal complexes, for example $[Ni\{(Ph_2PCH_2CH_2)_3N\}I]^+I^-$ (Fig 1.3).[23]

There are two limiting structures, the trigonal bipyramid and the square-based pyramid. The latter is rarely found for main group metals whereas both are known for transition metals. In pratice, the actual geometry observed is often a distortion of one of the two limiting structures. It is possible to group the variety of structures determined into five categories:

i) Regular trigonal bipyramid. Examples here include $Fe(CO)_5$[24] and the $[Pt(SnCl_3)_5]^{3-}$ ion.[25]

ii) Slightly distorted trigonal bipyramid. In these cases actual bond angles are often close to the regular values. There is true three-fold symmetry but the central atom may be a little out of the equatorial plane and the M-L distances may differ. A typical example is tris(2-diphenylphosphinoethyl)amino-nickel (II) iodide,[23,26] in which the nickel atom is displaced by 0.12Å from the equatorial plane, towards I. Independent bond lengths about the nickel atom are Ni-I=2.58, Ni-P=2.22 and Ni-N=2.28Å (Fig. 1.3).

iii) Highly distorted trigonal bipyramid. these can also be veiwed as highly distorted square pyramids. This structure is often found among Schiff base complexes for example N-β- diethylamineethyl-5-chlorosalicylaldimino-nickel (II)[27] (Fig. 1.4).

iv) "Regular" square pyramid. Definitive example where the central metal atom lies in the basal plane have never been observed with certainty. Probably the closest cases are the 1:1 adducts of stable square planar d^8 systems, such as $[Pd\{(Me_2As)_2C_6H_4\}X]^+$.[28]

v) Distorted square pyramid structures. Here the central metal atom lies out of the basal plane and inside the pyramid. These are quite common, and examples include $[Fe(S_2CNEt_2)_2Cl]$ in which the iron atom lies 0.63Å above the basal plane[29] and $[Co(OAsPh_2Me)_4(ClO_4)]ClO_4$ where the cobalt atom lies 0.32Å above the basal plane.[30]

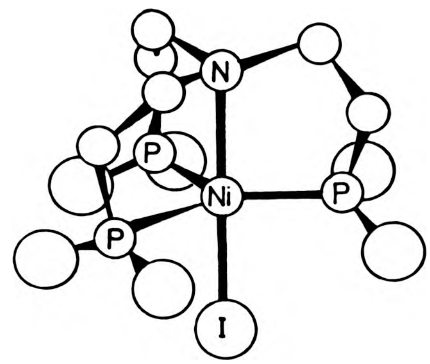


Fig. 1. 3 Structure of $[Ni\{(Ph_2PCH_2CH_2)_3N\}I]^+I^-$

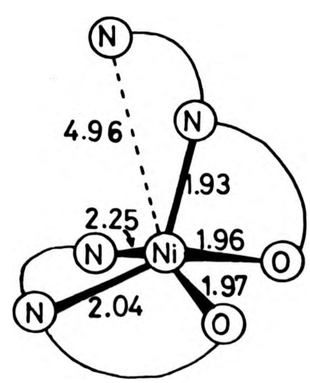


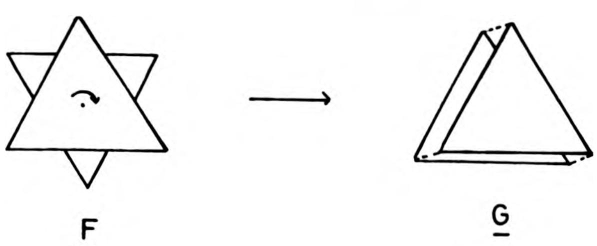
Fig. 1.4 Sketch of the molecular structure of $[5\text{-Cl-SALen}\,N(C_2H_5)_2]_2Ni$.

The actual geometry adopted depends on a variety of factors. The crystalline complex $[Cr(H_2N(CH_2)_2NH_2)_3][Ni(CN)_5].1.5H_2O$ is of interest as it contains two crystallographically independent $[Ni(CN)_5]^{3-}$ ions. One is a square pyramid with the nickel atom 0.34Å above the basal plane (Fig.1.5) and the other a distorted trigonal bipyramid [31] (Fig.1.6).

Coordination Number Six.

The octahedral situation is easily the most common geometry for six-coordinate complexes. In fact the report[32,33] of the crystal structure of the trigonal prismatic complex $[Re(S_2C_2Ph_2)_3]$, (Fig.1.7), in 1965, caused some surprise.

The stabilization of one six-coordinate geometry with respect to another will be the result of (a) maximising metal-ligand bonding interactions, (b) minimising all non-bonded contacts and (c) maximising bonding interactions between the atoms of the ligand itself.[34] Twisting of the octahedron (F) about the three fold axis results in the formation of a trigonal prism (G).



In the latter, the donor atoms are eclipsed, and consequently condition (b) is violated. This can only be relieved by lengthening the metal-ligand bond distances or by trigonal elongation, both of which violate condition (c). Therefore,

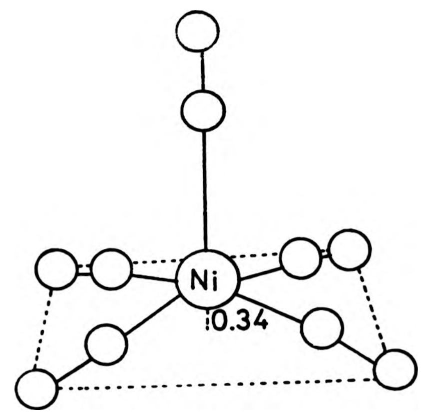


Fig. 1.5. Square pyramidal $[Ni(CN)_5]^{3-}$.

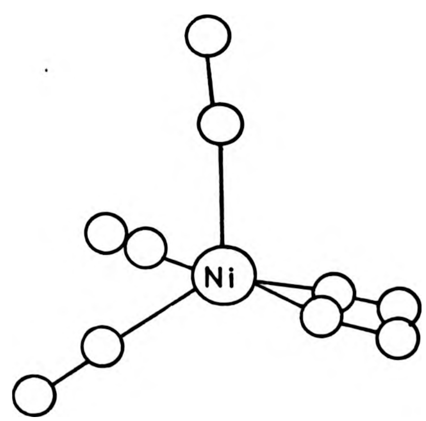


Fig. 1.6. Trigonal bipyramidal $[Ni(CN)_5]^{3-}$

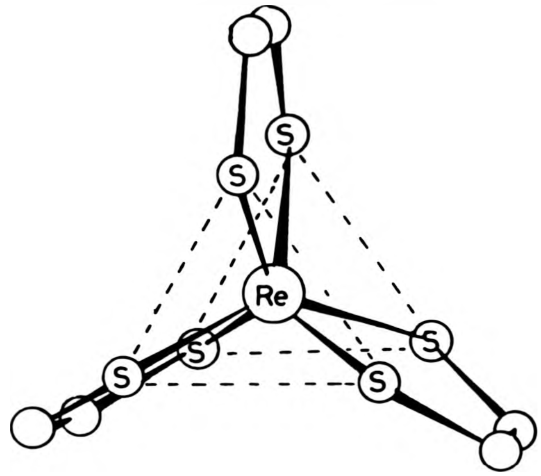


Fig. 1.7 Molecular structure of $[Re(S_2C_2Ph_2)_3]$.

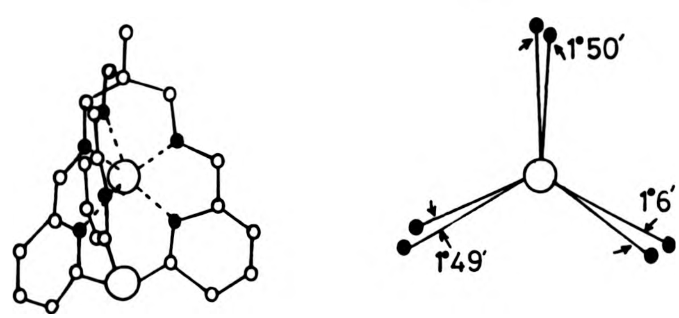
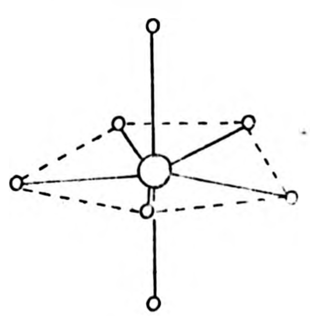


Fig. 1.8 Structure of $[\{FB(ONCHC_5H_3N)_3P\}Ni]^+$

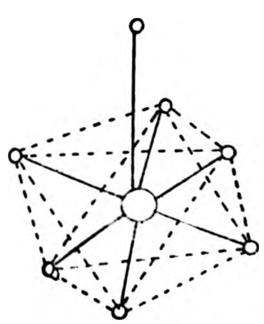
in most cases the octahedral stereochemistry is favoured over the trigonal prism. To stabilize the trigonal prismatic geometry a ligand is required which will maximise all bonding interactions and minimise all non-bonded contacts when in such a configuration [15,35]. To this end rigid, hexadentate ligands, capable of encapsulating a metal atom have been synthesised, eg. fluoroboro tris (2-aldoximo-6-pyridyl) phosphine.[36] The nickel (II) complex of this ligand has been prepared and shown to be practically trigonal prismatic with a twist angle of only 1.5°[37] (Fig.1.8). In these complexes a fine balance between the steric dictates of the ligand and the electronic nature of the central metal atom exists. In the iron (II) complex the balance is weighted towards electronic factors and a distorted structure with a twist angle of ~21° is observed[38].

Coordination Number Seven

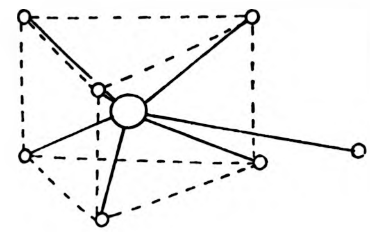
The majority of seven-coordinate complexes [39,40] can be described in terms of three polyhedra, pentagonal bipyramid (G), capped octahedron (H), and capped trigonal prism (I).



G

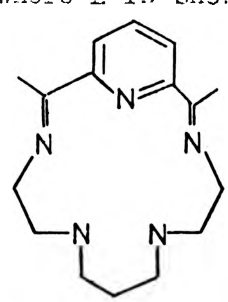


H



I

i) The pentagonal bipyramid. Here the axial sites are the least, while the equatorial sites are the most, crowded. Consequently, in most $[ML_7]$ cases the $M\text{-}L_{ax}$ bonds are shorter than the $M\text{-}L_{eq}$ bonds. Chelate ligands with small "bite" distances, such as nitrate, are well suited to occupy the equatorial positions. Planar pentadentate ligands have also been used to stabilise pentagonal bipyramidal structures by occupying the complete ring of equatorial sites, eg. $[FeL_5(NCS)_2]$[41] (Fig. 1.9), where L is shown below:-



ii) The capped octahedron. This is found most frequently in two types of compound:-

a) molybdenum (II) and tungsten (II) carbonyl halides with phosphorus and arsenic ligands, eg. dibromo-tricarbonyl 1,2 bis (diphenylphosphino) ethane molybdenum (II) -1-acetone.[42] (Fig 1.10)

b) $M(L\text{-}L)_3L$ complexes of the rare earth metals

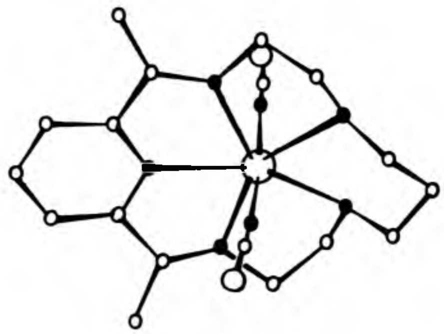


Fig. 1.9 Molecular structure of $[FeL_5(NCS)_2]$

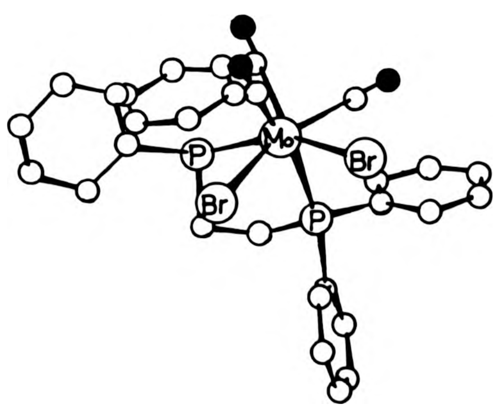


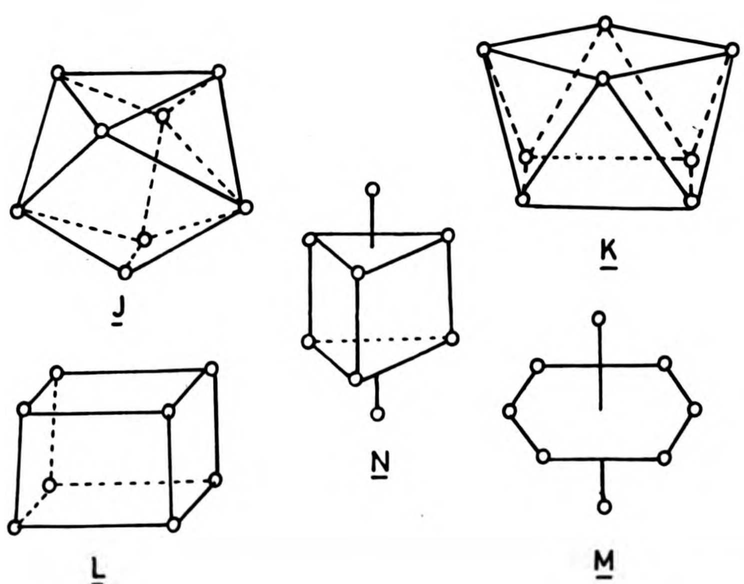
Fig. 1.10 Molecular structure of $[Mo\{Ph_2P(CH_2)_2PPh_2\}(CO)_3Br_2]$.

eg. $Ho(C_6H_5COCHCOC_6H_5)_3 . H_2O$.[43]

iii) The capped trigonal prism. This is more frequently found in polymeric structures, such as $Zr(SO_4)_2$,[44] than in monomers, although it has been found to be the preferred geometry for $[Mo(CNR)_7]^{2+}$ and $[Mo(CNR)_6X]^+$ complexes.[45] For example in heptakis-(tert-butyl isocyanide) molybdenum (II) hexafluorophosphate[46] the geometry of the $[Mo(CNR)_7]^{2+}$ cation is close to the idealised C_{2v} monocapped trigonal prismatic geometry.

Coordination Number Eight.

Several idealised geometries are possible for eight coordinate complexes,[39,47-50] the dodecahedron (J), square antiprism (K), the cube (L), the hexagonal bipyramid (M), and the bicapped trigonal prism (N).



The few examples of a bicapped trigonal prismatic arrangement tend to be grossly distorted. The cube and the hexagonal bipyramid are very rare; the former is known only in crystal lattices, and the latter in some uranyl complexes. In uranyl complexes hexagonal bipyramid structures are feasible because of the strength of the uranyl group and the large size of the uranium atom. Steric crowding sometimes forces the hexagonal girdle from planarity. Thus although the girdle is planar in the [UO_2(pyridine 2,6 dicarboxylate)] anion, [51] it is considerably puckered in the [UO_2(diethyldithiocarbamate)] anion. [52]

There is very little difference in interligand repulsions between the dodecahedron and the square antiprism. Slight bending motions may convert one into the other, in consequence intermediate geometries are also found. Of the numerous examples now known containing both the dodecahedron and square antiprism arrangements, by far the commonest are the type $[M(L-L)]^{n-}$, examples include the dodecahedral tetrakis-(oxalato) zirconium (IV) anion [53] and square antiprismatic zirconium (IV) acetylacetonate. [54]

The small energy difference between the dodecahedral and square antiprismatic arrangements makes it difficult to predict configurations. Thus the $[ZrF_8]^{4-}$ anion is dodecahedral in $Li_6(BeF_4)(ZrF_8)$ [55] (Fig 1.11) but square antiprismatic in $[Cu(H_2O)_6]_2[ZrF_8]$ [56] (Fig 1.12).

Coordination Number Nine and Higher

Nine-coordinate structures [39,49] are fairly common in

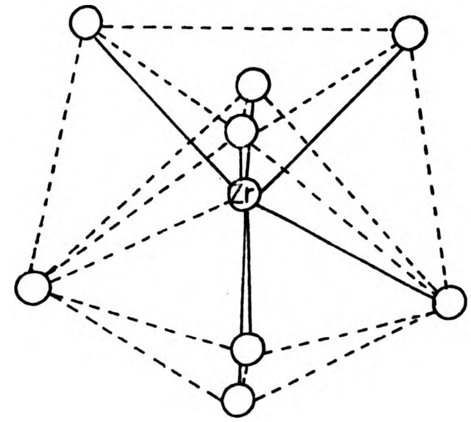


Fig. 1.11. Dodecahedral $[ZrF_8]^{4-}$.

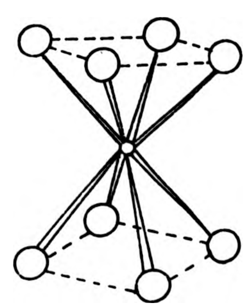
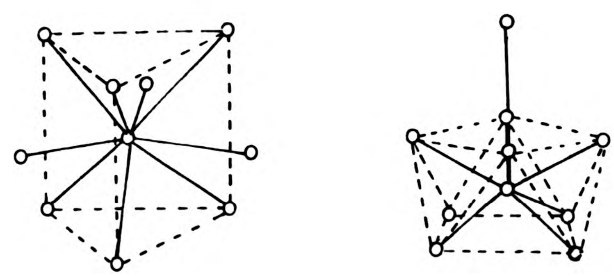


Fig. 1.12. Square Anti-prismatic $[ZrF_8]^{4-}$.

molecular complexes of the lanthanide and actinide ions but exceedingly rare with other metal ions. Nine-coordinate complexes are always described in terms of two ideal geometries, viz. the tricapped trigonal prism (P) or the capped square antiprism (Q).



P Q

All monomeric ML_9 type complexes known have tricapped trigonal prismatic structures, eg. the $[ReH_9]^{2-}$ ion in K_2ReH_9 [57] (Fig 1.13). Capped square antiprism arrangements are rare although a large number of complexes have been shown to have structures intermediate between this geometry and the tricapped trigonal prism.

Coordination numbers higher than nine are known but tend to be restricted to the lanthanides and actinides involving small monodentate ligands and chelate ligands with small bites, eg. $[Ho(NO_3)_5]^{2-}$ contains ten-coordinate holmium [58] and $[Th(NO_3)_6]^{2-}$ twelve-coordinate thorium.[59]

1C PHYSICAL TECHNIQUES

Unambiguous structural information may be obtained using

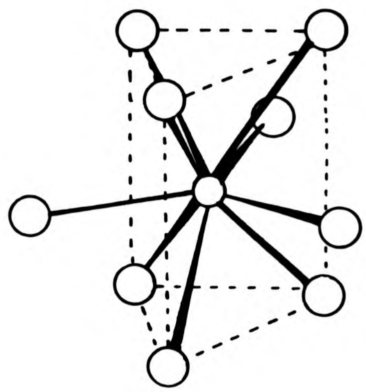


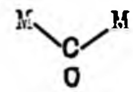
Fig 1.13 Tricapped trigonal prismatic $[ReH_9]^{2-}$.

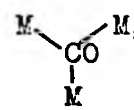
x-ray, neutron or electron diffraction methods. Literally thousands of structure determinations have been reported. However not all systems are amenable to this type of study, possibly because suitable crystalline materal cannot be obtained or decomposition occurs before the completion of data collection. Furthermore solid state structures may not be retained in other phases. However other physical techniques may also play a vital role in the determination of the structures of coordination compounds. They may also give valuable information about dynamic processes, which diffraction studies cannot. Several different techniques and their relevance to the research work described in this thesis will now be discussed.

Infra-red (I.R) Spectroscopy.

Metal carbonyls are an interesting group of compounds since the carbonyl ligands stabilize the metal in low oxidation states. The carbonyl groups are easily displaced, so that metal carbonyls are frequent precursors to other systems. Any carbonyl groups remaining often stabilize the molecule with respect to oxidation and/or thermal decomposition. Further they are useful probes to the electronic and molecular structure of the compound, as the C-O stretching vibrations are sensitive to environment.[60-64] The C-O stretching motion may be treated independently since the large energy difference between this vibration and the M-C stretching and M-C-O bending modes means there is no coupling between them. The carbonyl group can coordinate in three ways:

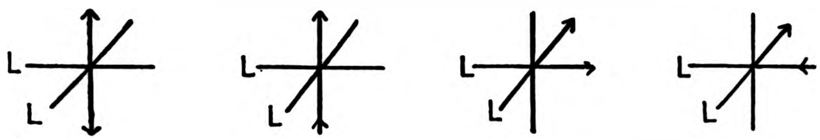
a) As a terminally bonded ligand, M-CO, as in $Fe(CO)_5$, with stretching frequencies in the region 2150 to 1800 cm^{-1}.

b) As a bridge between two metal atoms , as in $Fe_2(CO)_9$, with stretching frequencies occuring in the range 1850-1700 cm^{-1}.

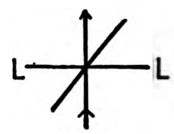
c) As a bridge between three metal atoms , as in $Rh_6(CO)_{16}$, with stretching frequencies as low as 1620 cm^{-1}.

It should be noted, that these are not necessarily limiting forms as intermediate bond types are known. The C-O stretching frequencies given are only meant as an approximate indication to position, since the presence of ligands without π-acceptor properties may force terminal carbonyl frequencies into the 'normal' bridging carbonyl range.

The number of infra-red active vibrations of a polyatomic molecule is related to the molecular symmetry.[65] Consider a molecule $L_2M(CO)_4$, which may exist as either cis- or trans-isomers. The cis-isomer has C_{2v} symmetry and four infra-red bands are predicted:-



Only one band is expected for the trans-isomer:-



The infra-red spectrum of $[Mo(CO)_4bipy]$ exhibits four carbonyl stretching bands at 2022, 1906, 1877 and 1826 cm^{-1} confirming that the two nitrogen atoms are coordinated in cis- positions. Whereas for the complex $[Mo(CO)_4(PMe_3)_2]$ only one strong absorption is observed at 1893 cm^{-1} indicating a trans arrangement.[66]

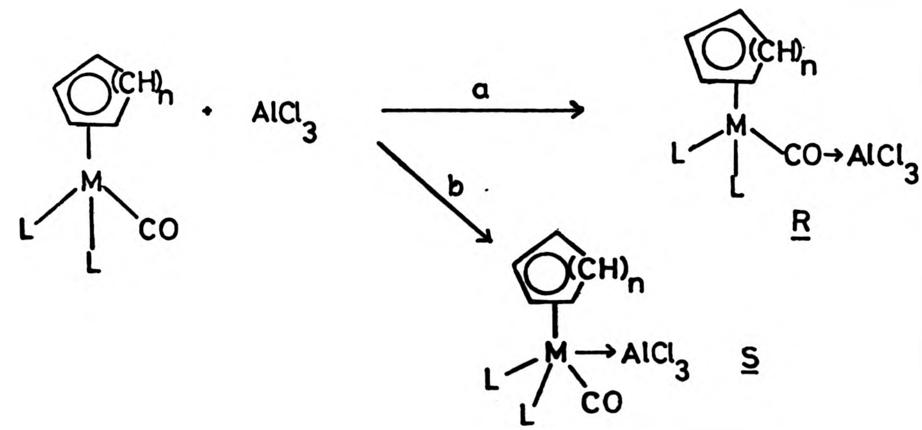
A number of other factors may affect the spectrum, eg. the presence of unsymmetrical ligands may lower the symmetry giving additional bands to those expected. Also bands may be missing through accidental degeneracy, poor resolution or weak intensity. Other types of ligands which have fundamental stretching frequencies in the carbonyl region include dinitrogen complexes ($\nu N\equiv N$), metal hydrides ($\nu M-H$) and metal nitrosyls ($\nu N\equiv O$). These points must be borne in mind when interpreting spectra.

From direct comparisons of ν(C-O) frequencies of related complexes certain qualitative conclusions may be drawn. Carbonyl stretching frequencies are dependent on the nature of any other ligands present and their ability to disperse electron density. They have been used as measures of the σ- and π- bonding capabilities of the other ligands. Electronegative substituents, such as halide ions or perfluoroalkyl groups, may raise the (C-O) frequency above that in unsubstituted carbonyls. Lewis bases, being less good π-acceptors than carbon monoxide, lower the frequency when they replace carbonyl groups. From the magnitudes of these effects orders of ligands with respect to their bonding ability have been discussed.[66-68] (Table 1.1)

Table 1.1 Carbonyl stretching frequencies in $ML(CO)_5$ complexes.[69]

Complex	ν(C-O) cm^{-1}			
	A_1	A_1	B_1	E
$Mo(PCl_3)(CO)_5$	2095	2001	....	1987
$Mo(PCl_2OEt)(CO)_5$	2091	1987	2012	1975
$Mo[P(OMe)_3](CO)_5$	2080	1967	1995	1950
$Mo(PPh_3)(CO)_5$	2078	1951	1990	1951
$Mo(PEt_3)(CO)_5$	2070	1941	1980	1948
$Mo(C_6H_{11}NH_2)(CO)_5$	2072	1895	1983	1938
$Mo(Me_2NCHO)(CO)_5$	2068	1847	....	1924

The position of the carbonyl stretching frequency has been used to characterize the products from the reaction of $AlCl_3$ with a variety of cyclopentadienyl and aryl carbonyl transition metal complexes. In these reactions two modes of adduct formation are possible:



On addition of $AlCl_3$ to $[(C_5H_5)Mn(CO)_3]$ in benzene a low frequency carbonyl stretching mode (1747cm^{-1}) is observed consistent with the formation of R . In dichloromethane, a third species was observed, exhibiting high frequency carbonyl bands (2080 and 2118 cm^{-1}). This was assigned to a product with attachment via the manganese atom (S). Similarly the 1:1 adduct of BF_3 with $[(Ph_3PC_5H_4)Mo(CO)_3]$ shows an increase in the number of carbonyl absorption bands which are also shifted to higher frequency.[71] Both observations are consistent with attachment to the metal (Table 1.2)

Far Infra-red Spectroscopy.

The low frequency infra-red region (500-100cm^{-1}) can be very important in the study of coordination compounds, since metal-ligands vibrations are generally found there.[66, 72-75] In particular, metal-halogen

Table 1.2 Carbonyl stretching frequencies of some Metal carbonyl complexes and their $AlCl_3$ or BF_3 adducts.

Complex	ν(CO) cm^{-1}
(C_5H_5) $Mn(CO)_3$	2025, 1938
(C_5H_5) $Mn(CO)_3.AlCl_3$ in benzene	2117 (w) 2056(s) 2025(vs) 2001(s) 1938(vs) 1747(s)
$(C_5H_5)Mn(CO)_3AlCl_3$ in CH_2Cl_2	2118(w) 2080(sh) 2059(s) 2025(vs) 2005(s) 1938(vs) 1743(s)
$(Ph_3PC_5H_4)$ $Mo(CO)_3$	1904 (s) 1808(vs) 1791(sh)
$(Ph_3PC_5H_4)$ $Mo(CO)_3.BF_3$	2016(w) 1993(sh) 1957(s) 1935(s) 1896(sh)

vibrations have been studied extensively and certain valuable trends and correlations have been discussed[76,77] (Table 1.3)

Table 1.3 Some factors determining the position of metal-halogen stretching vibrations.

Factors	Effect
Oxidation state of metal	Higher oxidation state-Higher frequency
Mass of metal and ligand	Larger mass - Lower frequency

Table 1.3 continued.

Coordination number of the metal	Higher coordination number- Lower frequency.
Counter-ion	Increased size of counter-ion -Decreased frequency.
Bridging or non-bridging ligand.	Non-bridging ligand at higher frequency than bridging.
Ligand field stabilization energy	Higher energy - Higher Frequency

a) Oxidation state. If the coordination number of the metal remains constant, the metal-halogen stretching frequencies generally increase as the oxidation number of the metal increases. This trend is exemplified in table 1.4

Table 1.4 Effect of oxidation state on (M-X) vibrations.

Compound	Stereochemistry	Oxidation state	ν(M-X) (cm^{-1})
IrF_6^{2-}	O_h	4	568
IrF_6^-	O_h	5	667
IrF_6	O_h	6	719

b) Mass effect. Since the frequency of a vibration is given by $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$, where μ is the reduced mass $\frac{m_1 m_2}{m_1+m_2}$, it follows that for heavier atoms the frequency will be lower, providing the force constant, k, is similar. (Table 1.5

Table 1.5 Effect of mass on ν(M-X) frequencies.

Compound	ν(M-X) (cm^{-1})
$MnCl_4^{2-}$	258, 249
$MnBr_4^{2-}$	195, 157
MnI_4^{2-}	116, 111
$TiCl_4(L-L)_2$ *	325, 317
$ZrCl_4(L-L)_2$ *	303, 295
$HfCl_4(L-L)_2$ *	281, 273

* (L-L) = o-phenylene bis(dimethylamine).

c) Coordination Number. In general, for a given oxidation state of a metal, the metal halogen stretching frequencies decrease as the coordination number of the metal increases. This reflects the general tendency for the longer bond lengths in metal complexes with higher coordination numbers. (Table 1.6)

d) Counter-ion effect. For a particular ion associated with different counter-ions, there is usually a shift in the fundamental frequencies. Some of the anion modes are more sensitive to change of cation than others.

However, in general the highest frequencies are found when the anion is associated with the smallest cation. (Table 1.7)

Table 1.6 Variation of ν(Ti-Cl) and (V-Cl) with coordination number.

Complex	Coordination Number	ν(M-Cl) (cm^{-1})
$TiCl_4$	4	490
$TiCl_4.2L$	6	380
$TiCl_4.2(L-L)$	8	317
VCl_4	4	482
$VCl_4.2L$	6	370
$VCl_4.2(L-L)$	8	317

Table 1.7 Variation of the infra-red active frequencies with cation for square planar $PtCl_4^{2-}$ complexes.

Cation	ν_2	ν_6	ν_7
K	175	325	193
Rb	167	320	190
Cs	160	316	185

e) Bridging vs non-bridging. It is generally accepted that bridging (M-X) frequencies are lower than terminal ones. However unequivocal assignments are not always possible in complexes containing both bridging and terminal metal-halogen bonds.

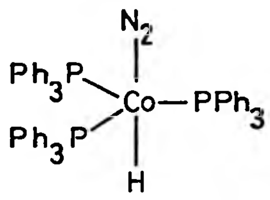
f) Ligand-field stabilization energy. It has been found that for the series of tetralkylammonium salts of MX_4^{2-} the ν(M-X) follows the same pattern as the order of ligand field stabilization energies, ie Mn<Fe<Co>Ni>Zn.

Nuclear Magnetic Resonance(N.M.R)Spectroscopy.

A wide variety of problems can be solved by using N.M.R. techniques,[78-81] with most instruments capable of studying ^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{31}P nuclei.

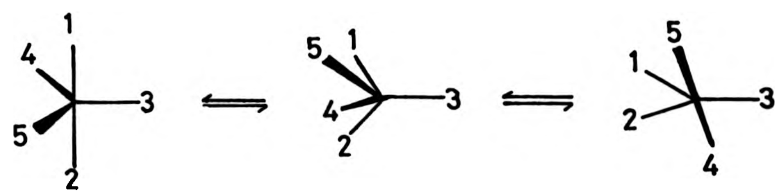
N.M.R.is particularly useful for the investigation of structures in solution. For rigid structures, ie. the nuclear configuration is maintained for a time that is large compared to the N.M.R. time scale, geometries can often be identified from examination of characteristic resonance frequencies and/or spin-spin fine structure. Fluxional molecules possess more than a single configuration representing an energy minimum, several such minima being possible and accessible with ordinary thermal energies. N.M.R. techniques have proved invaluable in the study of such fluxional molecules, and variable temperature experiments can often determine the nature of the dynamic process occuring in solution.[82,83]

The molecular dinitrogen complex $[HCoN_2(PPh_3)_3]$ is rigid on the N.M.R. time scale and its hydride resonance consists of a 1:3:3:1 quartet, suggesting coupling with three equivalent phosphorus nuclei. This is consistent with the thre phosphorus ligands occupying the equatorial positions of a trigonal bipyramid (T).[84]



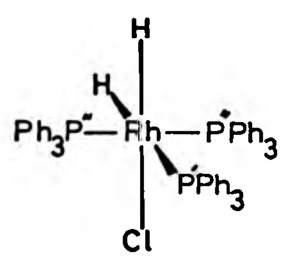
I

Infra-red and electron diffraction data has shown that PF_5 has a trigonal geometry but the ^{19}F N.M.R. spectrum consists of a single doublet down to 113K.[85] A fast intramolecular process must be occuring which exchanges equatorial and axial fluorines. The spin-spin coupling (J_{P-F}) is maintained discounting a dissociative mechanism. The accepted mechanism for the exchange process is Berry psuedorotation, with a square pyramidal transition state:-



This type of behaviour is a common feature of five-coordinate structures. The cationic five-coordinate complex $[Rh\{P(OMe)_3\}_5]^+$ is of interest as the rate of the exchange process may be reduced to a frequency that is low on the N.M.R. time scale at low temperatures, allowing unambiguous assignment of a trigonal bipyramidal structure.[86] The low temperature spectrum is complex and corresponds to a computer simulated spectrum for an A_2B_3X model. On warming the signals broaden, finally coalescing to give a sharp doublet, indicating the intramolecular exchange process.

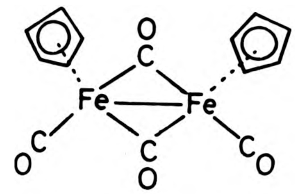
N.M.R. may also be used to study intermolecular exchange reactions. However this area has received much less attention. Consider the hydride complex $[H_2RhCl(PPh_3)_3]$, shown by ^1H and ^{31}P N.M.R. to have the structure U. The



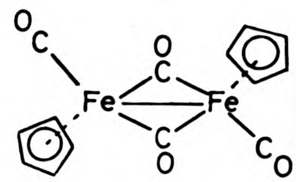
U

$^{31}P\{^1H\}$N.M.R. spectrum at low temperature exhibits a doublet of doublets for the phosphorus nuclei P" (split by Rh and by P') and a doublet of triplets for the nucleus P' (split by Rh and 2 P"). At high temperatures the P'-Rh and the P'-P" couplings are lost, while the P"-Rh coupling is retained. This shows that the P' ligand dissociates at an appreciable rate at the higher temperature.[87]

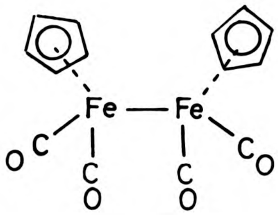
Metal carbonyl complexes are commonly fluxional, either by similar interconversions as discussed for the five coordinate complexes or via interconversion of terminal bridging carbonyl groups. The complex $[(C_5H_5)_2Fe(CO)_4]$ has been extensively studied with reference to the latter.[88] For this molecule three isomers are important (V, W, X).



V



W



X

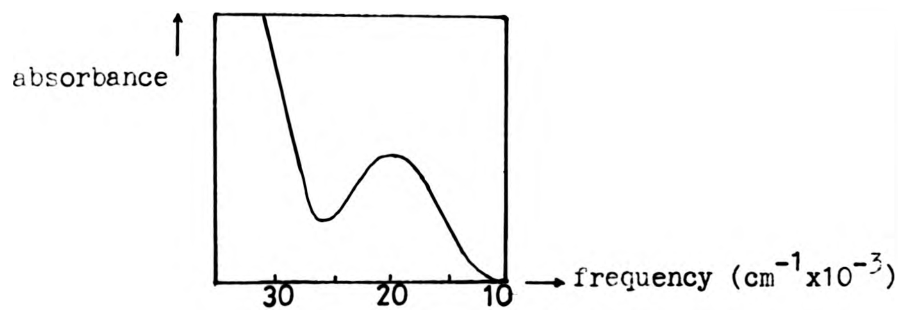
By oberserving the cyclopentadienyl proton resonances, it has been shown that the cis (V) and trans (W) bridged structures interconvert rapidly at room temperature. Below 223K the interconversion is slow enough to give separate proton N.M.R. signals. A variable temperature ^{13}C.N.M.R. study confirmed that this process occurs via the non-bridged isomer (X).[88-90]

Electronic Spectroscopy

It has long been realised that the electronic and stereochemical structure of a metal complex is reflected in its electronic spectra.[91,92]

Simplicistically, the five degenerate d-orbitals of a transition metal ion will lose their degeneracy when placed in a spatially non-uniform electric field, such as that generated by a set of ligands surrounding the ions. This is because the five d-orbitals are not spatially identical. Those that are in position to interact most with the ligands will increase in energy; the reverse is true for the others (Fig 1.14 and 1.15).

For the octahedral d^1 case, the d-electron will occupy the lowest energy orbital, ie, a t_{2g} orbital. Upon irradiation the ion may absorb sufficient energy to promote the electron to the upper e_g, level. The absorption band which results from this process is found in the visible spectrum of the hexaaquotitanium (III) ion and is responsible for its conspicuous violet colour.



Using the hole formalism the same discussion applies for d^9 ions. However with ions having d^2-d^8 electronic configurations this simple picture does not hold, a second interaction, between the electrons, also occurs. For these configurations energy-level diagrams based upon Russell-Saunders states, of the relevant d^n configuration are used. Just as the set of five d-orbitals is split by the electrostatic field of surrounding ligands, so are the various Russell-Saunders states of a d^n configuration (Table 1.8)

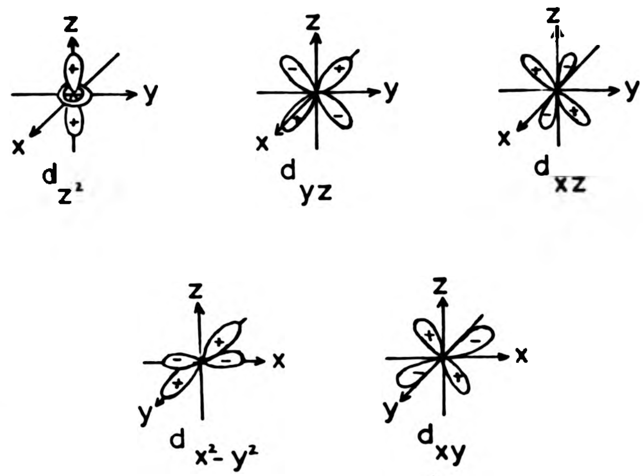


Fig. 1.14 Representation of d-orbitals.

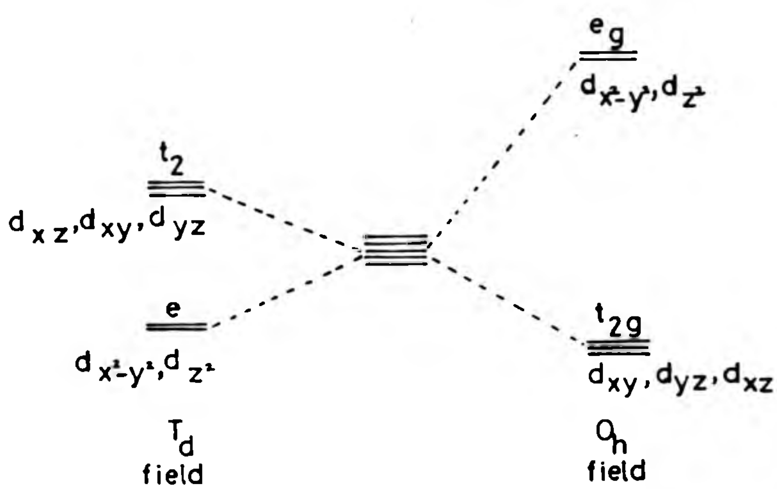


Fig. 1.15 d-orbital splitting in fields of T_d and O_h symmetry.

Table 1.8 Splitting of Russell-Saunders states in Octahedral and Tetrahedral Electrostatic Fields.

State of free ion	States in the crystal field
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$
H	$E + 2T_1 + T_2$

Although the states into which a free ion state are split are the same in number and type in both octahedral and tetrahedral fields, the pattern of energies is mutually inverted. Energy level diagrams for ions in electrostatic fields of various geometries have been drawn up by Orgel and by Tanabe and Sugano, for use in interpreting electronic spectra.[93,94] For a d^2 ion the complete energy level diagram is given in Fig 1.16. There is a quantum-mechanical selection rule that forbids transitions between states of different spin multiplicity, This means that in the present case only three transitions will occur, from the $^3T_1$ ground state to the three triplet excited states, $^3T_2$, $^3A_2$, and $^3T_1(P)$. This agrees with the spectrum observed for

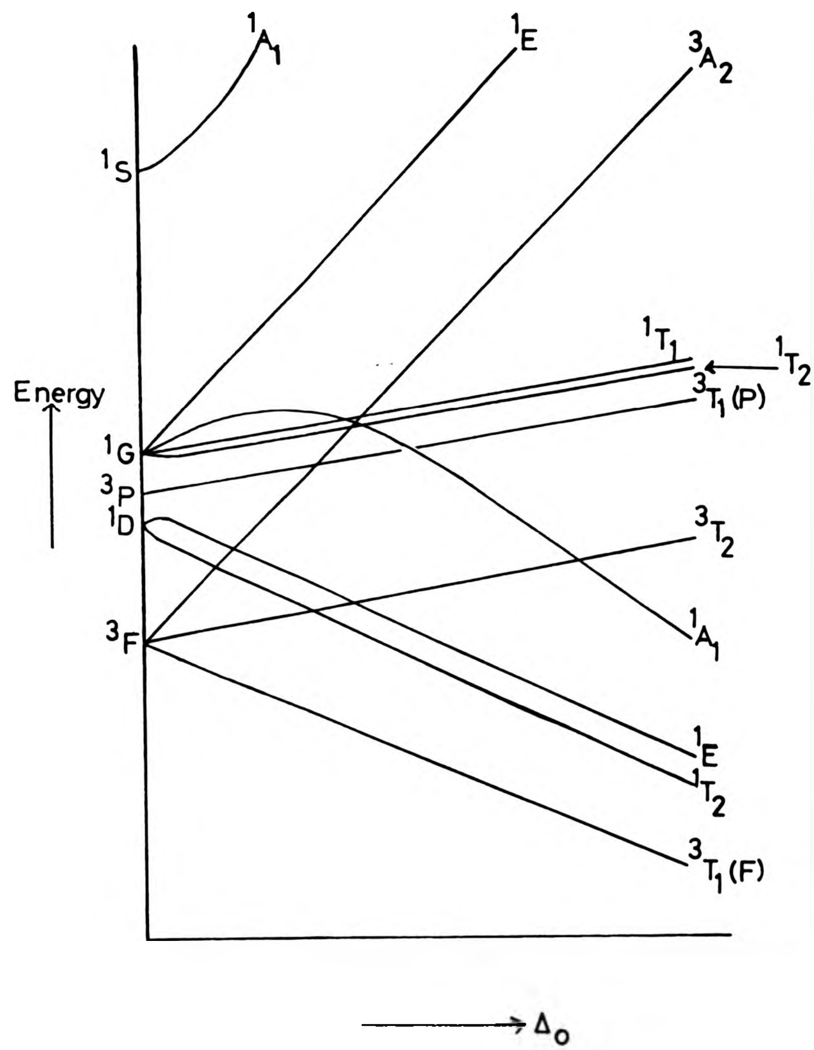


Fig. 1.16 Complete energy level diagram for the d^2 configuration in an octahedral crystal field.

$[V(H_2O)_6]^{3+}$ which contains three absorption at 17000, 25000, and 38000 cm^{-1}.

d-d electronic transitions are forbidden under the quantum-mechanical selection rules for light absorption. These rules may be stated as follows:-

a) Spin forbidden. Transitions in which there is a change in the number of unpaired electron spins are forbidden.

b) Orbitally forbidden. (Laporte rule). Transitions involving the redistribution of electrons in a single quantum shell are forbidden. However the Laporte selection rule may be relaxed, for centro-symmetric complexes by vibronic coupling and for asymmetric complexes by mixing of p and d orbitals.

Thus d-d transitions do occur but they are very weak.

Other electronic transitions may be observed in the electronic spectrum of a complex:-

a) Ligand spectra. Ligands such as water and organic molecules possess characteristic absorption bands. There are three types of ligand absorption :-

i) $n \rightarrow \sigma^*$. When atoms in molecules possess lone-pair electrons that are not involved in the internal bonding, the transition of lowest energy is $n \rightarrow \sigma^*$.

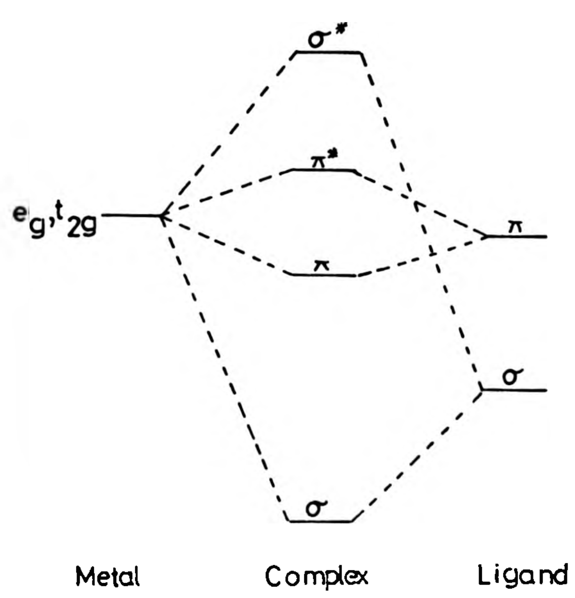
ii) $n \rightarrow \pi^*$. These transitions can occur in molecules containing atoms that are involved in π-bonding and that also contain non-bonding electron pairs.

iii) $\pi \rightarrow \pi^*$. Molecules possessing double or triple bonds but no atoms with non-bonding electrons have the π-

bonding orbital as the highest occupied level and the π^* as the lowest unoccupied level. The lowest energy transition is then $\pi \rightarrow \pi^*$.

b) Counter-ion Spectra. Absorption due to the counter-ion of a complex ion.

c) Charge-transfer Spectra. Electron transfer either from the ligand to the metal or vice-versa. Metal-Metal charge transfer is also possible in complexes containing two metal ions with variable valencies, and is termed mixed-valence or inter-valence transfer. Charge transfer bands are usually very intense and they account for the colour of d^0 complexes such as $TiCl_6^{2-}$ and CrO_4^{2-}. A simplified molecular orbital diagram for the hexa-halo complexes TiX_6^{2-} (X=Cl,Br) is given below:-



The σ and π levels are filled with bonding electrons while the π and σ^* levels are vacant.

For $TiCl_6^{2-}$ transitions assigned to $\pi \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ are observed at 31850 and 42500 cm^{-1} respectively. For $TiBr_6^{2-}$ they occur at 25200 and 36500 cm^{-1} respectively.[95]

Mass Spectrometry.

Metal carbonyls are well suited to studies by mass spectrometry because of their volatility, often symmetrical geometries, and their readiness to lose ligands in consecutive steps with little further fragmentation. The main advantages offered by this technique is the rapid determination of accurate molecular weights and molecular formulae, but other information may also be obtained. Binuclear and polynuclear metal carbonyls have been studied with particular reference to the possibility of metal-metal bonding. When there is a strong interaction between the metal centres, eg. $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Ru_3(CO)_{12}$, high abundances of ions containing the metal-metal bonds intact are observed. Compounds in which there is a weaker interaction, eg. $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, produce far fewer ions containing M-M bonded species.[96-99] (Table 1.9)

Identification of the number of hydrogen atoms in metal hydrides often involves major difficulties. Accurate molecular weight determinations and consideration of isotope peak patterns associated with an ion can lead to assignment of molecular formulae for such compounds. For example the mass spectrum[100] of $[H_3Re_3(CO)_{12}]$ confirms the formulation as a trimeric hydride.

Table 1.9 Relative abundances of metal containing ions for some polynuclear metal carbonyls.

Compound	$M_3(CO)_m^+$	$M_2(CO)_n^+$	$M(CO)_p^+$
$Mn_2(CO)_{10}$		59	41
$Co_2(CO)_8$		75	25
$Ru_3(CO)_{12}$	93	5	2
$Fe_2(CO)_9$		0	100
$Fe_3(CO)_{12}$	36	4	60

The parent molecular ion $[H_3Re_3(CO)_{12}]^+$ is observed and furthermore, the isotopic pattern is consistent with the presence of three rhenium atoms per molecular ion.

Other Physical Techniques

Other physical techniques which may be useful in the study of coordination compounds, include Raman,[101] electron spin resonance (E.S.R.) [102], and Mossbauer spectroscopy [103] but these will not be discussed in any detail here.

Raman Spectroscopy. Raman spectroscopy is similar to infra-red in that it is concerned with vibrational and rotational transitions. The selection rules, however, are different. In order for a vibration to be Raman active, the change in polarizability of the molecule with respect to vibrational motion must not be zero at the equilibrium position of the normal vibration. Since the selection rules are different, the information obtained sometimes complements that obtained from infra-red study.

Electron Spin Resonance. E.S.R. is a branch of absorption spectroscopy in which radiation of microwave frequency is absorbed by molecules possessing electrons with unpaired spins. For an electron of spin $s=\frac{1}{2}$, the spin angular momentum quantum number can have values of $M_s = \pm \frac{1}{2}$, which in the absence of a magnetic field are degenerate. On application of a magnetic field the degeneracy is resolved. Transitions between the two different electron spin energy states occurs upon absorption of a quantum of radiation in the radio-frequency or microwave regions. The energy of the transitions is given by:

$$E = h\nu = g\beta H_o$$

The quantity, g, the spectroscopic splitting factor, is not a constant but depends upon the orientation of the molecule containing the unpaired electron with respect to the magnetic field.

When an unpaired electron comes in the vicinity of a nucleus with a spin I, an interaction takes place which causes the absorption signal to be split into (2I+1) components. If the electron is delocalized over several nuclei the splitting caused is more complex. For an electron delocalized over a set of n equivalent nuclei of spin I_n and a set of m equivalent nuclei of spin I_m the number of lines is given by $(2nI_n+1)(2mI_m+1)$. Thus for the methyl radical four lines are observed.[104]

Mossbauer Spectroscopy. Mossbauer spectroscopy involves nuclear transitions which result from the absorption of γ-rays by the sample. The conditions for absorption depend upon the electron density about the nucleus and the number of peaks obtained is related to the symmetry of the compound. Although the Mossbauer effect has been observed for about one-third of the elements, only for iron and to a lesser extent tin has it been a major research tool for the chemist.

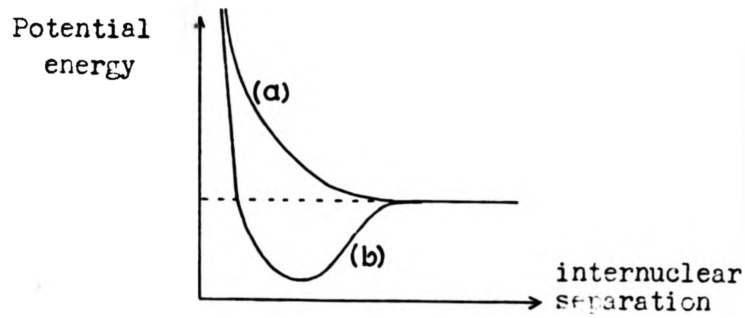
1D BONDING IN COORDINATION COMPLEXES.

There are three main bonding models which have been used in inorganic chemistry, the valence bond (V.B.) approximation, the molecular orbital (M.O.) theory and the crystal-field theory (C.F.T.).

Valence Bond Theory.

The valence bond theory[105] grew out of the ideas of electron pairing put forward by Lewis. The premise that chemical bonds are due to the sharing of one or more pairs of electrons is the basis of the theory. The valence bond approximation is an attempt to invest these qualitative ideas with quantum-mechanical validity. The bond formation is treated from the stand point of the pairing of electron spins and the maximum overlapping of atomic orbitals containing these electrons to give a region of common electron density to the combining atoms.

In the hydrogen molecule, as the two hydrogen nuclei approach each other from an infinite distance the weak attractive forces are gradually opposed by strong repulsive forces at short interatomic distances. Interaction between the wave functions of the electrons occurs, if the electrons have parallel spins their energy continues to rise as the atoms get closer together and no bond forms (a).



If the spins are opposed, however, the energy curve possesses a definite minimum which corresponds to the formation of a stable molecule (b).

In heteroatomic molecules, covalent bond formation may be considered as the pairing of electron spins by approach and overlap of atomic orbtals of suitable energy and symmetry. The strongest bonds are formed when maximum interaction of electron density is effected. More than one orbital from each atom may be employed in bond formation. In the V.B. approach this is called hybridization. The hybrid orbitals, formed by the mixing of atomic orbitals, have characteristic directions in space. (Table 1.10)

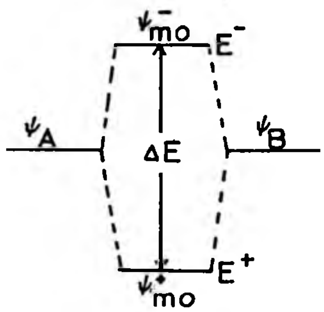
The valence bond theory gives no understanding of electronic spectra and consequently molecular orbital and crystal field theories are more useful to the transition metal chemist.

Table 1.10 Directional properties of some hybrid orbitals.

Coordination Number	Hybridisation	Orbitals used	Stereochemistry
2	sp	s, p_z	Linear
2	dp	d_{z^2}, p_z	"
3	sp^2	s, p_x, p_z	Trigonal planar
4	dsp^2	$d_{x^2-y^2}, s, p_x, p_y$	Square planar
4	sp^3	s, p_x, p_y, p_z	Tetrahedral
4	sd^3	$s, d_{xy}, d_{xz}, d_{yz}$	"
5	dsp^3	$d_{z^2}, s, p_x, p_y, p_z$	Trigonal bipyramidal
6	d^2sp^3	$d_{x^2-y^2}, d_{z^2}, s, p_x, p_y, p_z$	Octahedral

Molecular Orbital Theory.

Molecular orbital theory[106] differs basically from the valence bond approach in that it takes into consideration all the electrons of the combined atoms and considers these to be jointly held by the molecule in a set of polynuclear orbitals. It is not possible to derive the polynuclear molecular orbitals by solving the Schrödinger wave equation for that system. Consequently some approximations concerning the form of the wave function for the molecular orbitals must be made. This can be acheived by using linear combinations of atomic orbitals (L.C.A.O). The combination of two atomic orbitals results in the formation of two molecular orbitals, the difference in energy of which is related to the effective overlap between the two orbitals:-



antibonding orbital

bonding orbital

Maximum overlap will be obtained by combining atomic orbitals which are closest matched in energy and symmetry. Orbitals which are not capable of effective overlap are termed non-bonding as they do not help or hinder bonding to any significant extent.

Consider the simple M.O. approach to an octahedral complex. Of the nine valence shell atomic orbital for the metal only six have lobes pointing towards the corners of an octahedron;

$3d_{x^2-y^2}$, $3d_{z^2}$, 4s, $4p_x$, $4p_y$ and $4p_z$.

The σ valence orbitals of the ligand will, of course, vary from ligand to ligand but they will frequently be composed of s and p atomic orbitals; they can be represented as lobes (Fig 1.17). In order to construct an energy-level diagram for the ML_6 complex it is necessary to know the relative energies of the combining atomic orbitals. For first-row complexes 3d<4s<4p, and for most ligands, eg. H_2O, NH_3 and F^-, the σ_L orbitals used for bonding to the metal are lower in

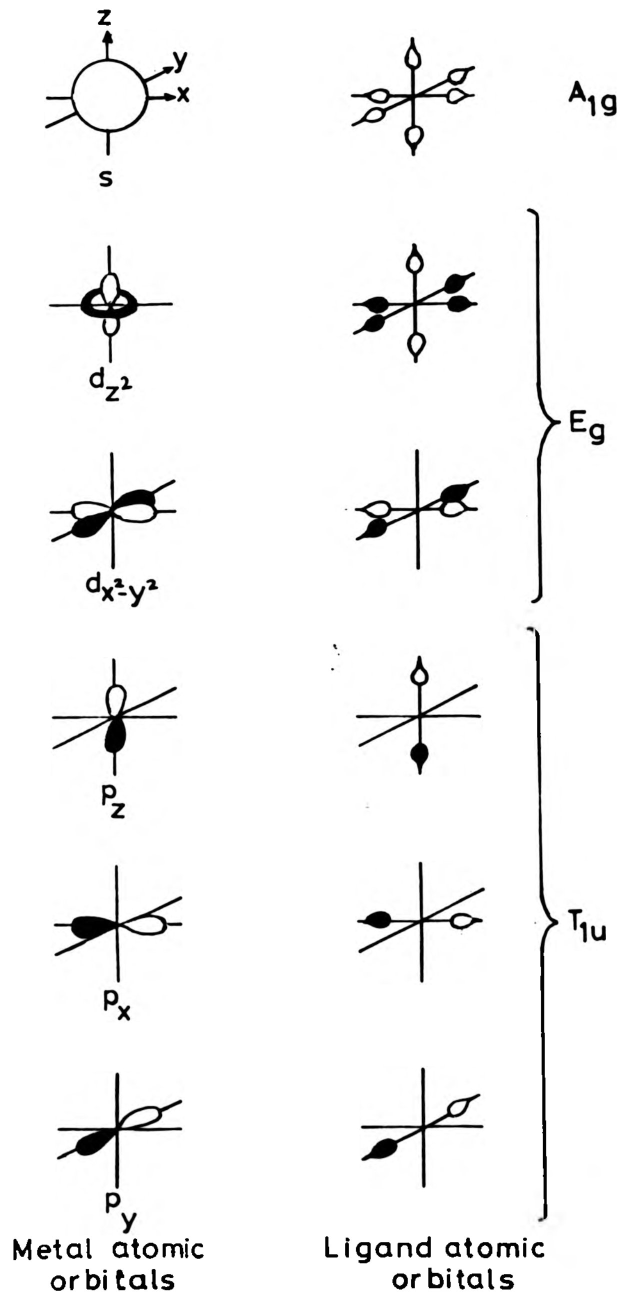


Fig. 1.17 The metal orbitals and their matching ligand group orbitals for an octahedral σ-bonded complex.

energy than the metal valence orbitals. The energy-level diagram for the complex can then be drawn up (Fig 1.18). In order to apply this diagram to a particular complex, the six pairs of electrons from the ligands are placed in the lowest energy levels (two to each level). Any valence shell electrons in the metal ion are therefore placed in the t_{2g} and e_g^* orbitals.

Molecular orbital energy-level diagrams can be constructed in a similar way for other stereochemistries. Contributions from π-bonding can also be taken into account. As well as giving a satisfactory explanation of magnetic data, molecular orbital energy-level diagrams account for the electronic spectra of complexes.

Crystal Field Theory.

In molecular orbital theory covalent bonding is of prime importance. Crystal field theory starts at the opposite extreme, dealing with electrostatic interactions.

There is no unique way of representing the five d-orbitals but the most convenient representations are shown in Fig 1.14. Crystal field theory assumes that the only interaction between the metal ion and the ligands is an electrostatic one. The five d-orbitals in an isolated gaseous metal ion are degenerate. In a complex the ligands take up certain positions in space. The d-orbitals directed towards the ligands will be raised in energy as a result of the repulsion between the negative electrons of the orbitals and the negative field generated by the ligands. The energy of those orbitals not

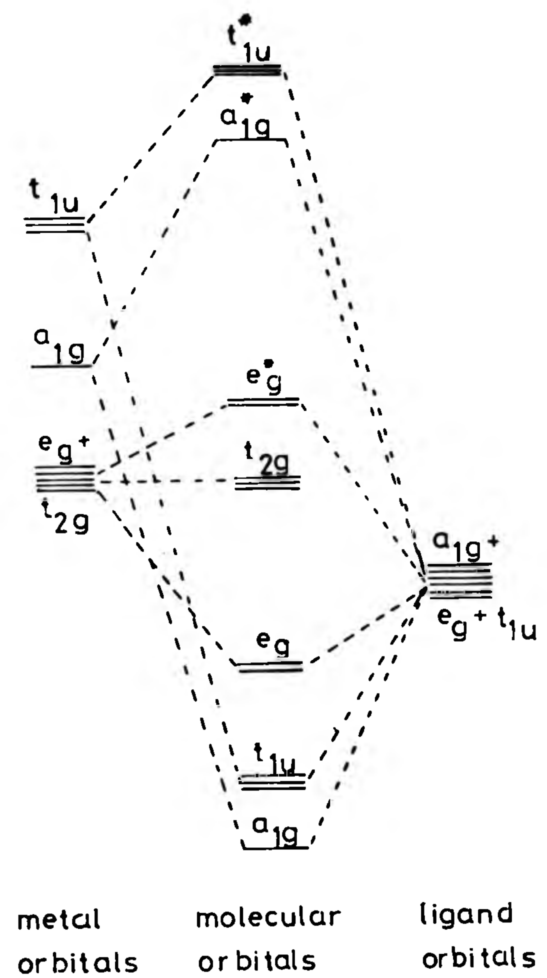
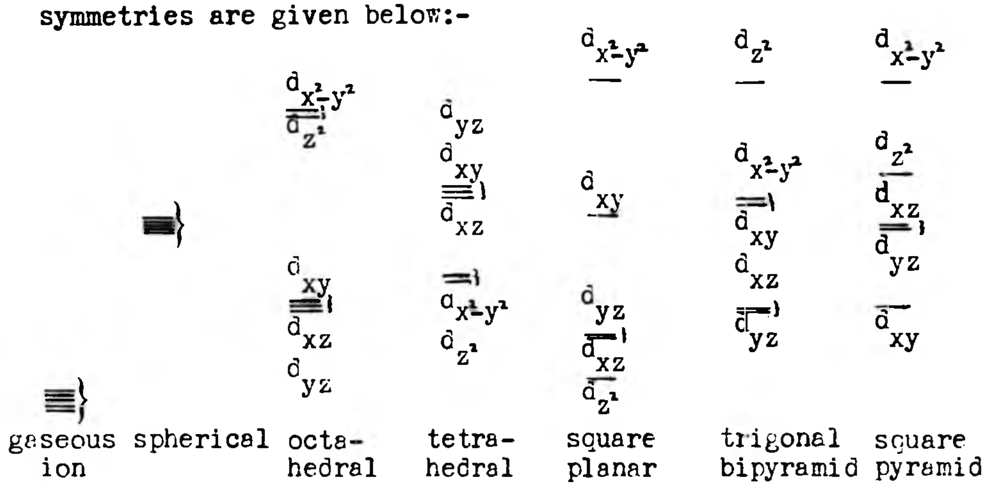


Fig. 1.18 Molecular orbital diagram for an octahedral ML_6 complex.

directed towards the ligands will also increase but not as much as the others. Splittings for fields of various symmetries are given below:-



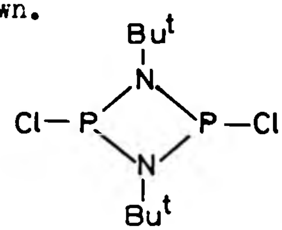
Crystal field theory adequately explains the magnetic properties of transition metal complexes, and the electronic spectra of d^1 and d^9 ions. With more than one electron in the d-shell interaction between the electrons also has to be taken into account. Energy-level diagrams based upon the splitting of the Russell-Saunders states in the appropriate ligand field are used. (For a brief discussion of this see the section on electronic spectra.)

CHAPTER TWO.

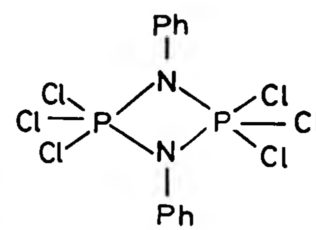
CHEMISTRY OF THE 1.3.2.4 DIAZADIPHOSPHETIDINES.

INTRODUCTION.

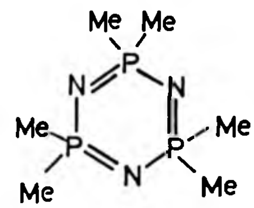
Until recently very few examples of heterocycles containing alternate trivalent phosphorus and nitrogen atoms, based on structures of type (I) or larger sizes, had been reported.[107] In contrast, the types (II) and (III) are well known.



I



II



III

The nomenclature used in the literature for these rings is varied, for example compounds of type (I) have been termed cyclodiphosphazanes, dimeric phosphazo-compounds and 1,3,2,4, diazadiphosphetidines. A summary of the I.U.P.A.C. recommendations[108] on the nomenclature of heterocyclic systems is noted below, and will be followed in this thesis.

Nomenclature for fundamental heterocyclic systems.

Monocyclic compounds containing one or more hetero atoms in a three to ten membered ring are named by combining the appropriate prefix or prefixes from Table 2.1 (eliding "a" where necessary) with a stem from Table 2.2. The state of hydrogenation is indicated either in the stem as shown in table 2.2 or by the prefixes "dihydro-", "tetrahydro-" etc.

Table 2.1 Prefixes for naming heterocyclic systems.

Element	Valence	Prefix
Oxygen	II	Oxa
Sulphur	II	Thia
Selenium	II	Selena
Tellurium	II	Tellura
Nitrogen	III	Aza
Phosphorus	III	Phospha*
Arsenic	III	Arsa*
Antimony	III	Stiba*
Bismuth	III	Bisma
Silicon	IV	Sila
Germanium	IV	Germa
Tin	IV	Stanna
Lead	IV	Plumba
Mercury	IV	Mercura

*When immediately followed by "in" or "ine", "phospha" should be replaced by "phosphor" "arsa" by "arsen" and "stiba" by "antimon".

For pentavalent phosphorus atoms the prefix λ^5 will be used, eg. $(ClPNMe)_2$; 1,3 dimethyl 2,4 dichloro 1,3,2,4-diazadiphosphetidine, $(Cl_3PNMe)_2$; 1,3 dimethyl 2,2,2,4,4,4 -hexachloro 1,3,2λ^5,4λ^5 diazadiphosphetidine.

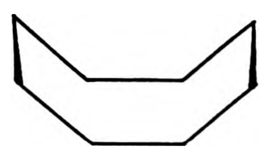
Table 2.2 Stems for naming heterocyclic systems.

Ring size	Rings with nitrogen		Rings without nitrogen	
	Unsaturated	Saturated	Unsaturated	Saturated
3	-irine	-iridine	-irene	-irane
4	-ete	-etidine	-ete	-etane
5	-ole	-olidine	-ole	-olane
6	-ine	*	-ine	-ane
7	-epine	*	-epine	-epane
8	-ocine	*	-ocin	-ocane
9	-onine	*	-onin	-onane
10	-ecine	*	-ecin	-ecane

* expressed by prefixing "perhydro" to the name of the corresponding unsaturated compound.

The best known of the phosphorus nitrogen heterocycles are those of general formula $(X_2PN)_n$ in which four-coordinate phosphorus atoms alternate with nitrogen atoms such rings with n=3 to 17 have been reported.[109-112]

The chloro derivatives$(Cl_2PN)_n$ were probably first prepared in the 1830's, independently by Rose and by Leibig and Woehler, from phosphorus pentachloride and ammonium chloride, but correct compositions, molecular weights etc. did not follow until later. The cyclic nature of these compounds was not proved until some 65 years later, when Stokes isolated 6 to 14 membered rings. More recently x-ray diffraction studies have supplied much structural data.[113] The trimers consist of planar six-membered rings, whereas higher ring sizes are more flexible, for example the tetramers are generally isolated in either the 'tub' (A) or 'crown' (B) forms.



A **B**

Exceptions, however, include $(F_2PN)_4$ and $(Cl_2PN)_5$ which are planar.

In general the P-N bonds are equal and are shorter than comparable single P-N bonds indicating some sort of delocalisation. Two different explanations of the type of bonding have been advanced:-

a) $p\pi - d\pi$ aromatic delocalisation within the ring.[114,115]

b) allylic type (insular) delocalisation within P-N-P fragments of the ring.[116,117]

The chloro derivatives are readily prepared:-

$$PCl_5 + NH_4Cl \xrightarrow{140-150^\circ} \frac{1}{n}(Cl_2PN)_n + 4HCl$$

The major product is the trimer, smaller amounts of the tetramer and higher oligomers can be isolated. Not only were these chloro derivatives the first of these class of compounds to be prepared but they are also the most useful as the precursors of other derivatives. For example arylated derivatives can be obtained by a Freidel-Crafts arylation:-[118-120]

$$(Cl_2PN)_3 + nPhH \xrightarrow{AlCl_3} (Ph_nCl_{6-n}P_3N_3) + nHCl$$

$$n = 2, 4 \text{ or } 6$$

They may also be obtained directly:[121-123]

$$PhPCl_4 + NH_4Cl \longrightarrow \frac{1}{n}(ClPhPN)_n + 4HCl$$

$$n = 3, 4$$

Alkoxy, aroxy, amino and alkylthio derivatives are easily prepared by substitution:-[124,125]

$$(Cl_2PN)_3 + R_nXH \xrightarrow{Et_3N} [(R_nX)_2PN]_3 + 2Et_3NHCl$$

$$R_nX = MeO-, EtO-, \tfrac{1}{2}O-, Me_2N-, Et_2N-, \text{etc}$$

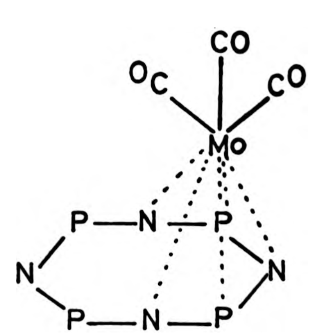
and

$$(Cl_2PN)_3 + 6NaSEt \longrightarrow [(EtS)_2PN]_3 + 6NaCl$$

Metal complexes have been obtained, for example with metal carbonyls :-[126]

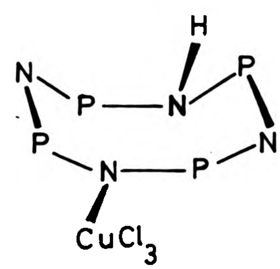
$$(Me_2PN)_4 + Mo(CO)_6 \longrightarrow [(Me_2PN)_4]Mo(CO)_4 + 2CO$$

An x-ray crystal structure[127] analysis showed the P_4N_4 ring to be approximately planar and the molybdenum atom to be within bonding distance of a 5 atom (N-P-N-P-N) chain but out of range of the remaining (P-N-P) set (C).



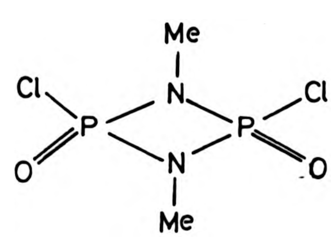
C

Similar 1:1 complexes of $(Me_2PN)_3$ with $SnCl_4$ and $TiCl_4$ were proposed to be σ-complexes with donation from one or two nitrogen sites.[128] With the six-membered ring $(Cl_2PN)_3$, three carbonyls are replaced from chromium hexa-carbonyl, and an essentially arene-type complex is proposed.[129] In contrast $CoCl_2$ and $CuCl_2$ give ionic complexes, $[(NPMe_2)_4H]_2^+ CoCl_4^{2-}$ and $[(NPMe_2)_4H]^+CuCl_3$.[130] In the latter the ring has a 'tub' conformation with a proton and a $CuCl_3$ group covalently bound to opposite nitrogens.(D)

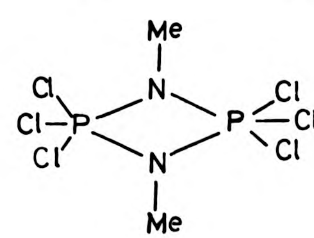


D

There are many examples of phosphorus-nitrogen heterocycles in which the nitrogen atoms are tricoordinate and the phosphorus atoms either four (E) or five (F) coordinate.

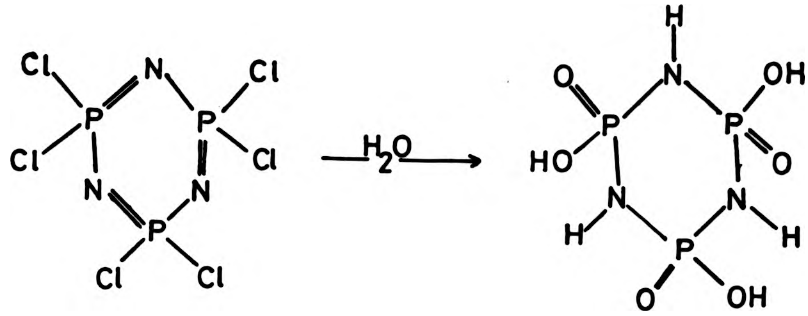


E

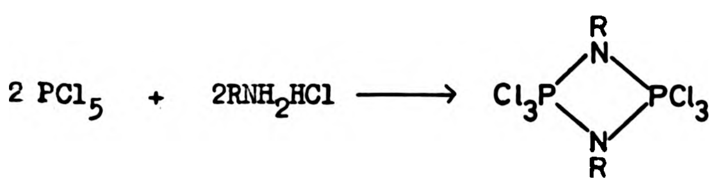


F

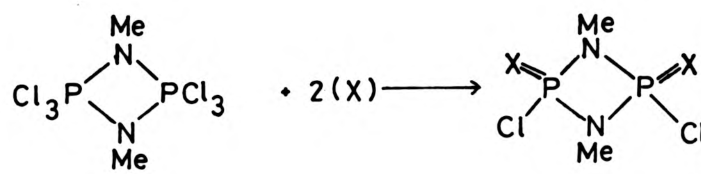
Most examples of type (F) are dimers however with type (E) larger ring sizes are known since they can be prepared by hydrolysis of the $(X_2PN)_n$ rings.[131]



The simplest and most general method for the synthesis[132] of 1,3 dialkyl or 1,3 diaryl 2,2,2,4,4,4 - hexachloro 1,3,2 λ^5, 4 λ^5 diazadiphosphetidines is the reaction of PCl_5 with primary aliphatic amines or the hydrochlorides of aliphatic or aromatic amines:-



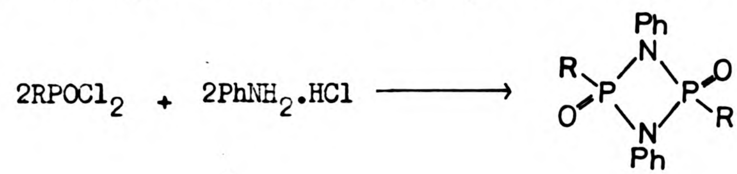
The white crystalline products are readily hydrolysed by atmospheric moisture, and have a tendency to depolymerise on heating. Very few substitution reactions which preserve the phosphorus-nitrogen ring have been acheived, EF_3(E=As,Sb) will convert the hexachloro derivatives to the hexafluoro derivatives. Conversion to four-coordinate phosphorus rings is acheived on treatment with SO_2 or H_2S:-



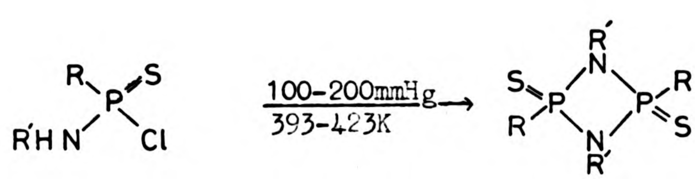
where $(X) = \frac{1}{2}\ SO_2,\ X = O$

$(X) = H_2S\ ,\ X = S$

These heterocycles may also be prepared directly :-

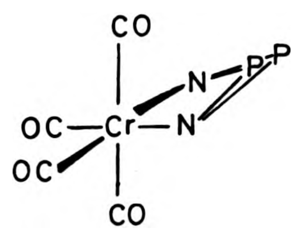


and similarly the dithio derivatives :-



1,3,2 λ^5,4 λ^5 diazadiphosphetidines with the tetra-coordinate phosphorus atoms are fairly stable, but may be attacked by nucleophilic reagents with labile hydrogen atoms, such as water, phenols, amines etc.

Few metal complexes have been investigated. A chromium carbonyl complex has been isolated,[133] in which $(MeNPCl_3)_2$ was proposed to act as a bidentate nitrogen donor to a $Cr(CO)_4$ unit (G).



G

Similarly $(Me(S)PNCl)_2$ gives a 1:1 complex with $TiCl_4$ in which bidentate nitrogen donation was proposed.[134]

Historically formation of four membered $[P(III)N]_2$ heterocycles, from the reaction of PCl_3 with an excess of a primary amine, was first proposed at the turn of the century.[135] Spasmodic reports followed, corroborating this formulation but it was not until 1969 that confirmation was obtained by an x-ray crystallographic study [141,142] of $(ClPNBu^t)_2$, the product of the reaction sequence:-[143]

$$2Bu^tNHSiMe_3 + 2Bu^nLi \longrightarrow 2(Me_3Si)Bu^tNLi \xrightarrow{2PCl_3} \longrightarrow (Bu^tNPCl)_2$$

Since then a large number of reports [144-170] concerned with the preparations, physical and chemical properties of these compounds have appeared in the literature.

A variety of routes (Fig 2.1) have been utilised to prepare 1,3,2,4 diazadiphosphetidines, most of which involve the reaction of PX_3 (X=halide) with an amine or amine derivative, for example:-

i) $4\ Bu^tNH_2 + 2\ PCl_3 \longrightarrow (Bu^tNPCl)_2 + 2\ Bu^tNH_2.HCl$

ii) $PhN(SiMe_3)_2 + PhN(PCl_2)_2 \longrightarrow (PhNPCl)_2 + 2\ Me_3SiCl$

iii) $MeP(NHBu^t)_2 + PCl_3 + 2py \longrightarrow (Bu^tNPCl)_2 + 2py.HCl$

The rings themselves are easily ruptured by nucleophilic reagents (Fig 2.2), with water, phosphorous acid and the amine hydrochloride are formed:-

$H_2O + (ClPNBu^t)_2 \longrightarrow 2\,H_3PO_3 + 2Bu^tNH_2.HCl$

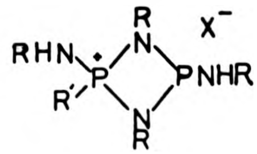
Reaction of organic acids with 1,3 diamino 1,3,2,4-diazadiphosphetidines yields carboxylic acid amides:-

$(RNHPNR)_2 + 2\ R'COOH \longrightarrow 2\ H_3PO_3 + 2R'CONHR$

1,3,2,4 diazadiphoshetidines will also undergo substitution reactions with alkaline nucleophilic reagents, thus with sodium alkoxides[171]:-

$(PhNPCl)_2 + 2\ EtONa \longrightarrow (PhNPOEt)_2 + 2NaCl$

They may also enter into addition reactions with electrophilic reagents via the unshared electron pairs:-

$(RNHPNR)_2 + R'X \longrightarrow$ 

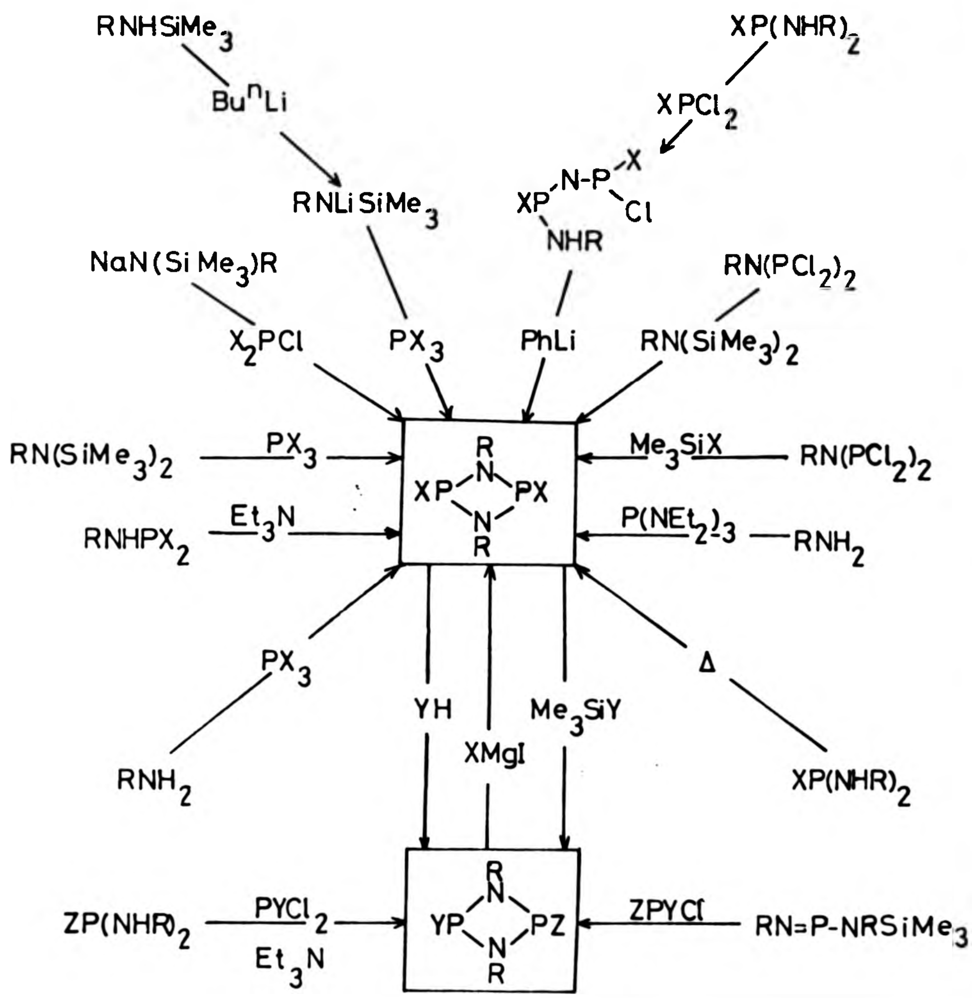


Fig. 2.1 Some preparative routes to the diazadiphosphetidine rings.

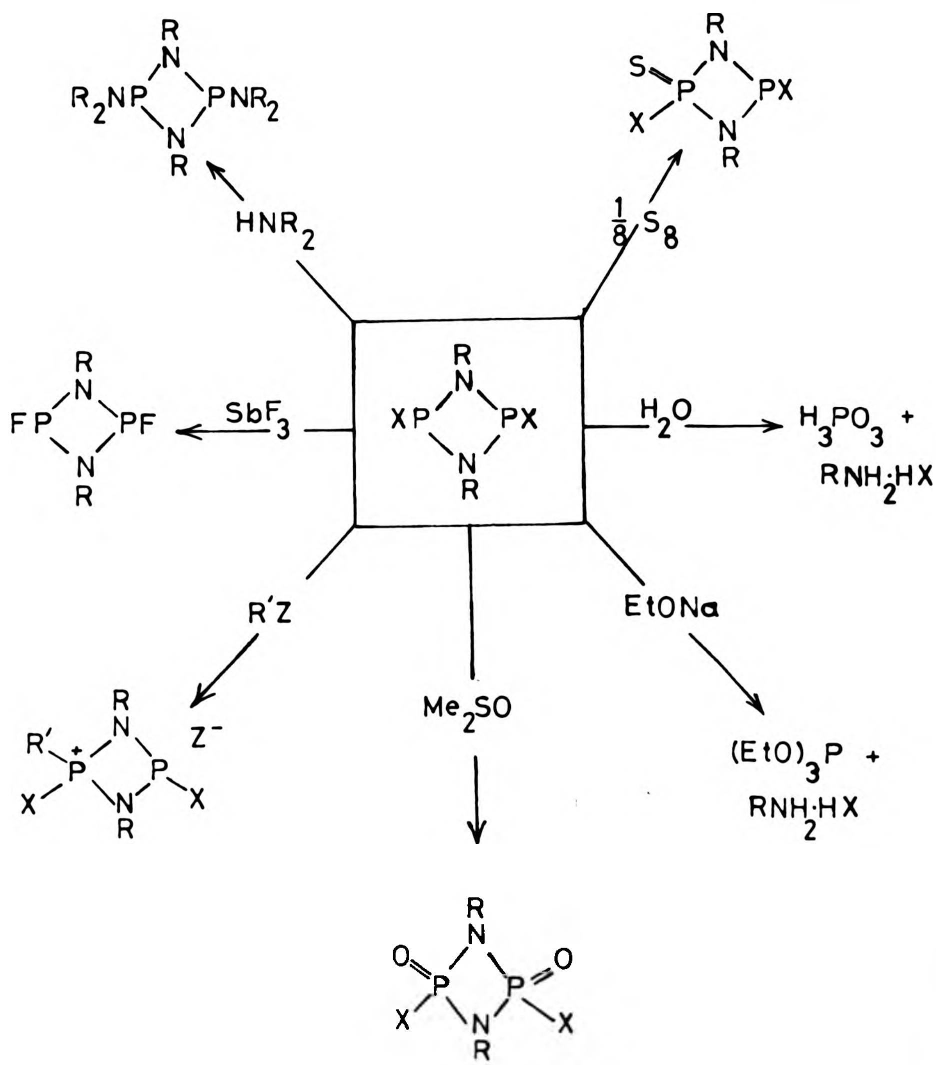
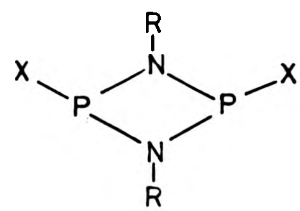


Fig. 2.2   Some reactions of the diazadiphosphetidine ring system.

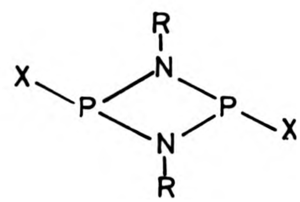
They are easily oxidised to give the 1,3,2 λ^3, $4\lambda^5$ and 1,3,2λ^5, $4\lambda^5$ diazadiphosphetidines[166]:-

$$(ClPNBu^t)_2 \; + \tfrac{1}{4}\, S_8 \longrightarrow (Cl(S)PNBu^t)_2$$

Two conformations are possible in the 1,3,2,4-diazadiphosphetidines, in which the exocyclic phosphorus substituents are either mutually cis- (H) or trans- (J), the nitrogen atoms being essentially planar.



H



J

X-ray crystal structure determinations have shown the P_2N_2 ring to be planar in trans - 1,3,2,4 diazadiphosphetidines (Fig 2.3) but tends to be puckered in the cis-isomers[142,143,153,164,170] (Fig 2.4 and 2.5). Similar behaviour has been noted for the 1,3,2λ^5,4λ^5 diazadiphosphetidines.[172-174] Mean P-N bond lengths in the (P (III)N)$_2$ rings are all somewhat shorter than that where the P-N bond is thought to be single in character (c.f. 1.769 Å in $[H_3NPO_3]^-$ [175]). Some delocalization of the nitrogen lone pairs onto the phosphorus atoms has been proposed to account for this. Particularly, for $(ClPNBu^t)_2$, the value of 1.689Å is in close agreement to that found in the open chain compounds

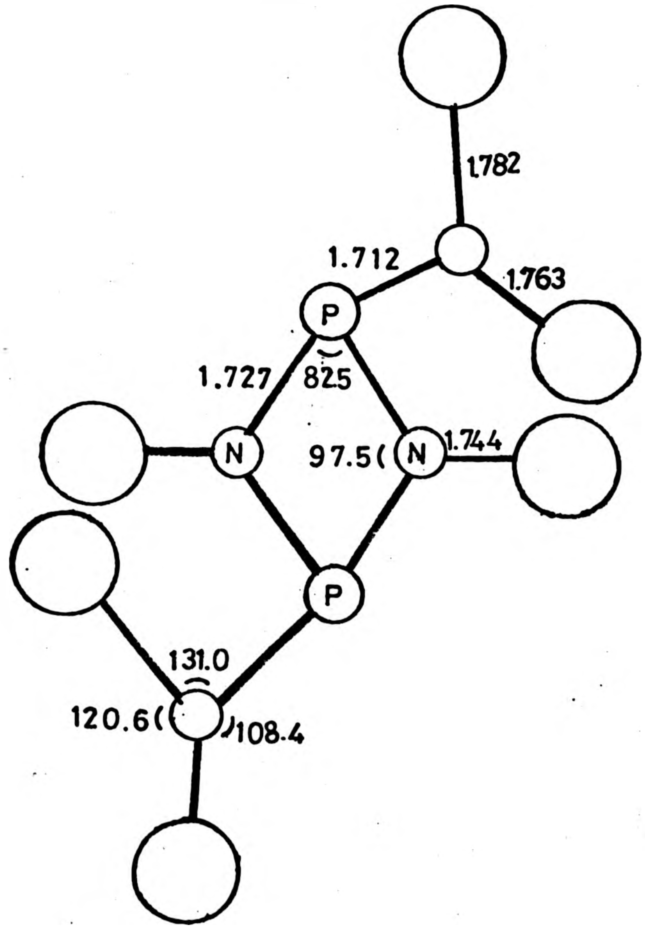


Fig. 2.3 Molecular structure of 1,3, bis(trimethylsilyl) trans-2,4, bis [bis(trimethylsilyl)amino] 1,3,2,4,-diazadiphosphetidine.

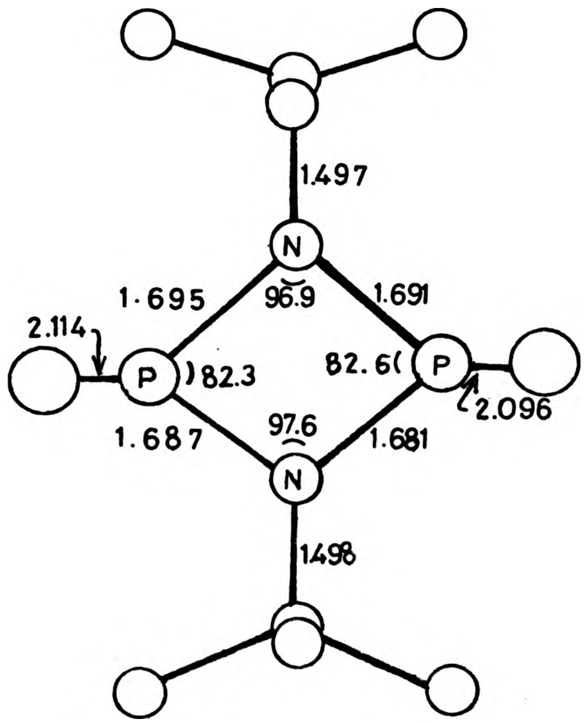


Fig. 2.4 1,3,di(tert.-butyl) cis-2,4, dichloro-1,3,2,4, diazadiphosphetidine viewed down the normal to the $[P-N]_2$ ring.

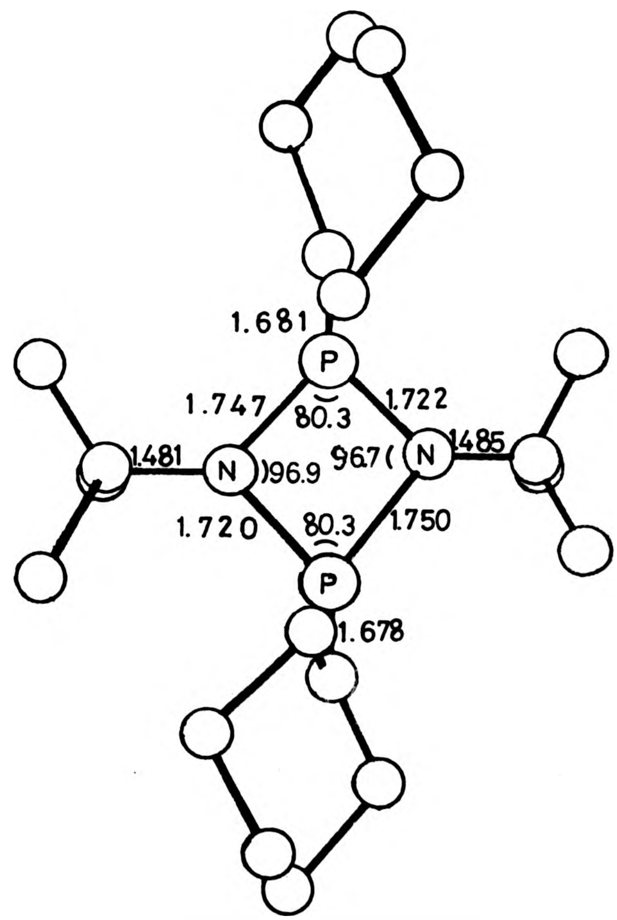


Fig. 2.5. A view of the 1,3 di(tert-butyl) cis-2,4,-dipiperidino 1,3,2,4, diazadiphosphetidine

Me_2NPCl_2 (1.69Å) and $(Me_2N)_3P$ (1.70Å) where the nitrogen lone-pair is believed to participate in (p-d)π bonding.[143] Delocalization, however, is not as great as in the unsaturated, $(XP^{V} \dot{=} N)_n$ rings which contain a formal double bond, where distances as short as 1.51Å have been observed.[176]

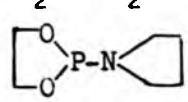
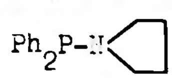
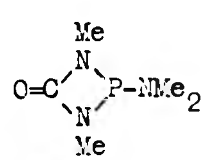
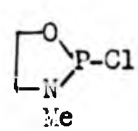
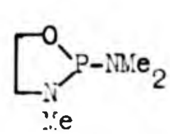
Infra-red data for these heterocycles is now fairly extensive but there have been few attempts at assignments. Group frequency correlations for phosphorus containing compounds have been compiled[177-179] (Table 2.3)

Table 2.3 Group frequency correlations for phosphorus bonds.

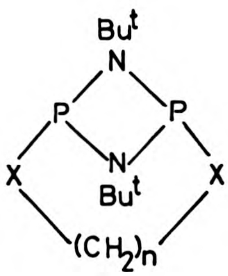
Bond	Range of frequencies (cm^{-1})	
	Double bonds	Single bonds
P-H		2500-2220
P-B	1480-1410	750-550
P-C	1390-1000	780-620
P-N	1500-1055	1100-790
P-O	1415-1100	1200-850
P-F		965-720
P-Si		515-380
P-P		510-340
P-S	860-515	615-440
P-Cl		610-400
P-Se	600-420	480-440
P-Br		495-320
P-I		350-290

The (P-N) stretching frequency for trivalent phosphorus compounds has been reported [180] over the considerable range 1010- 790 cm^{-1} (Table 2.4).

<u>Table 2.4 (P-N) Stretching frequencies in diverse P(III)N compounds</u>.

Compound	ν(P-N) (cm^{-1})
$P(NMe_2)_3$	951,935
$MeP(NMe_2)_2$	971,952
$(MeO)P(NMe_2)_3$	967,948
$Ph_2P(NMe_2)$	968
$Cl_2P(NMe_2)$	978
	1005
	1003
	977,905
	930
	960,922

For dithio derivatives, bands in the region 900-850cm^{-1} have been attributed to antisymmetric vibrations of the four-membered rings.[132] Keat and Thompson[159] assigned the bands at 900-850 cm^{-1} to ν_{as}(PNP) for the bicyclic compounds (K).



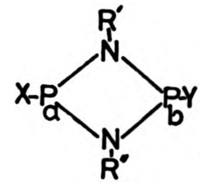
X= MeN, n= 2

X= O, n= 2,3

K

In contrast there is a wealth of ^{31}P.N.M.R. data for these compounds (Table 2.5) and their derivatives (Table 2.6). It should be noted that resonance signals which appear to high field (Lower frequency) of the reference (H_3PO_4) are given positive δ values. This is the reverse of the convention normally used for ^{1}H.N.M.R. From the tabulated data, it is evident that the ^{31}P chemical shifts move dramatically upfield on either increasing coordination number or valency of the phosphorus atoms. ^{31}P.N.M.R. can, therefore be used as a very sensitive indicator as to the environment around the phosphorus atoms. There is even a sizeable difference between the chemical shifts of two geometrical isomers,[158] where the lowfield isomer exhibits shifts generally much further downfield than expected for aminophosphines,

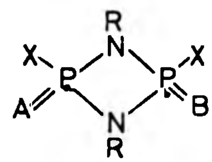
Table 2.5 ^{31}P.N.M.R. Spectral data for some 1,3,2,4 - diazaphosphetidines:



X	Y	R'	R"	Chemical Shift		Ref.
				P_a	P_b	
Cl	Cl	Bu^t	Bu^t	-210.9		149
F	F	Bu^t	Bu^t	-164		147
Cl	F	Bu^t	Bu^t	-197.1	-180.3	
OMe	OMe	Bu^t	Bu^t	-133.7		168
				-202.4		
NMe_2	NMe_2	Bu^t	Bu^t	-95.0		161
				-184.7		
Me	Me	Bu^t	Bu^t	-171.4		155
Bu^t	Bu^t	Me	Me	-281.7		157
				-201.7		
NMe_2	NMe_2	Ph	Ph	-101.0		161
				-166.5		
Cl	Me	Bu^t	Bu^t	-200.4	-237.0	155
Cl	OMe	Bu^t	Bu^t	-188.7	-139.4	168
Cl	NMe_2	Bu^t	Bu^t	-186.6	-131.5	168

Table 2.6 ^{31}P.N.M.R. spectral data for some selected derivatives of the 1,3,2,4 diazadiphosphetidines

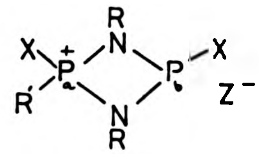
i)of the type

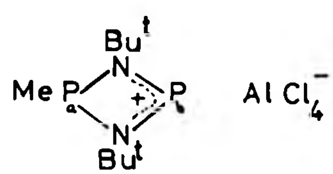


X	R	A	B	Chemical shift		Ref.
				P_a	P_b	
Cl	Bu^t	O	lone pair	-6.2	-132.4	151
Cl	Bu^t	S	lone pair	-61.1	-146.9	151
Cl	Bu^t	O	S	+3.6	-36.0	151
Me	Bu^t	O	O	-17.8		155
Me	Bu^t	S	S	-71.7		155
Me	Bu^t	Se	Se	-68.5		155
				-70.5		
Me	Bu^t	Te	Te	-36.0		155
Me	Bu^t	$NSiMe_3$	$NSiMe_3$	+10.8		
Bu^t	Me	S	S	-105.9		157
				-120.1		

Table 2.6 continued

ii)of the type



X	Z	R	R'	Chemical shift		Ref.
				P_a	P_b	
Me	Br	Bu^t	Me	-91.9	-195.0	155
Me	I	Bu^t	Me	-93.6	-193.4	155
NMe_2	I	$SiMe_3$	Me	-33.5	-92.2	167
				-54.3	-127.3	
iii) 				-201.0	-252.0	155

$P(NR_2)_3$. The contrast between the two isomers is sometimes reflected in their differing reactivity and physical properties.[164] The ^{31}P.N.M.R. data indicates that the thermodynamically favoured isomer is not the same with N-alkyl as with N-aryl substituents. In the former the high field isomer predominates, the reverse is observed for the latter. A crystal structure determination[164] has shown the thermodynamically favoured isomer of 1,3 di (tert-butyl) 2,4, dipiperidino 1,3,2,4 diazadiphosphetidine, which has a highfield chemical shift, to have a cis-configuration.

The mass spectra of several 1,3,2,4 diazadiphosphetidines $(XPNR)_2$ where R=alkyl or aryl have been studied[158] and indicate that the monomer (XP=NR) is not as effectively stabilised with N-alkyl substituents as with N-aryl substituents. (Table 2.7)

In stark contrast for $R=SiMe_3$, $X=R_2N$, no evidence for the presence of the monomers could be found, the main peaks in the mass spectrum being assigned[166] to ions of the following series:-

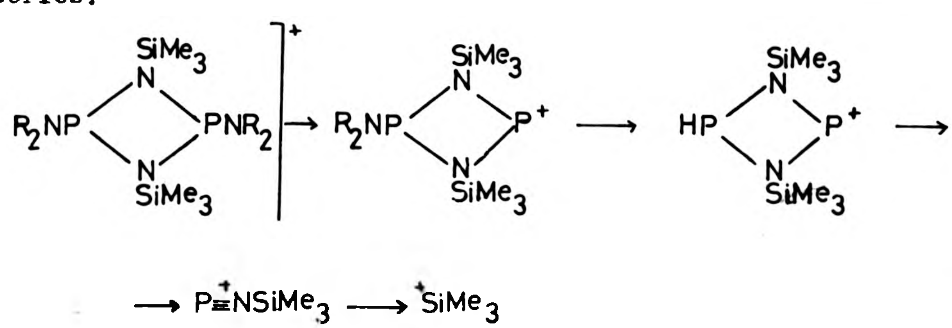
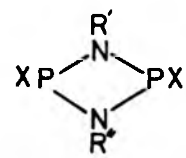


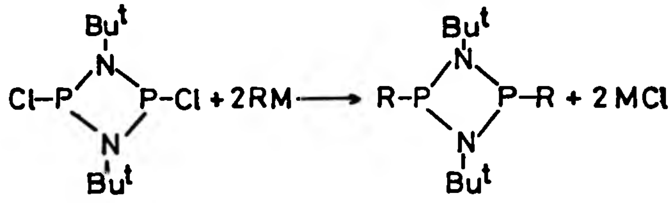
Table 2.7 Relative intensity of parent and (RNPX) ions in the mass spectra of the 1,3,2,4 diazadiphosphetidines.



R′	R″	X	$\frac{[M^+]}{[R'NPX^+]}$
Bu^t	Me	Cl	7.60
Bu^t	Bu^t	NEt_2	5.12
Bu^t	Bu^t	NMe_2	3.17
Bu^t	Et	Cl	1.82
Ph	Ph	NMe_2	0.73
Ph	Ph	Cl	0.36
$C_6H_4Cl_p$	$C_6H_4Cl_p$	Cl	0.04

Our study of the chemistry of the 1,3,2,4 diazadiphosphetidines can be conveniently divided into two sections:-

A. Halide replacement reactions, as a route to new 1,3,2,4 diazadiphosphetidines.



B. Coordination behaviour with various metal centres. By suitable choice of metal it was hoped to obtain examples of coordination via the ring phosphorus and/ or nitrogen.atoms.

EXPERIMENTAL

Preparation and purification of starting materials and manipulative details are described in Appendix A. All experiments were carried out under an inert atmosphere.

2A. Halide Replacement Reactions of 1,3 di(tert-butyl) 2,4 dichloro 1,3,2,4 diazadiphosphetidine.

2Ai With Butyl lithium

Bu^nLi ($36cm^3$ of 1.8 ml^{-1} hexane solution; 64.8m mols.) was slowly dripped into a solution of $(ClPNBu^t)_2$ (8.99_g;32.6 m mols) in hexane, at 273K. After removal of the LiCl precipitated, by filtration, the solution was fractionally distilled to yield the product, $(Bu^nPNBu^t)_2$ as a straw coloured, viscous liquid (bpt395K at 0.35mm Hg: 6.85g : 66%)

Infra-red Data (cm^{-1} ; liquid film) 3220(w) 2960(s) 2930(s,sh) 2900(s,sh) 2870(s) 2850(m,sh) 2810(w,sh) 2785(w,sh) 2710(w) 2600(w) 2500(w) 1628(w) 1460(s) 1385(m) 1375(m) 1360(s) 1345(w,sh) 1295(w) 1240(s) 1140(w) 1120(w) 1055(m,sh) 1035(s) 1000(s) 975(s) 924(m) 890(s) 850(s) 805(w) 790(m) 765(w) 740(w,sh) 730(w) 710(w,sh) 700(w,sh) 635(w) 600(w) 575(m) 540(vw) 480(m) 430(w) 395(w) 345(w) 290(w,br)

^{1}H.N.M.R. Data (δppm; ref TMS; $CDCl_3$solution) 0.93(2) 1.13(9) 1.22(1) 1.29(3) 1.32(2) 1.38(1)

^{31}P.N.M.R Data (δ ppm; ref H_3PO_4; $CDCl_3$ solution) -178.82

^{13}C.N.M.R.Data (δ ppm; ref TMS; $CDCl_3$ solution) 10.53(3) 15.01(3) 17.55 (10)

<u>Mass Spectrum</u> M^+: 318 (($Bu^nPNBu^t)_2$:318)

<u>2Aii With Methyl lithium</u>

MeLi ($17cm^3$ of $1.7ml^{-1}$ Et_2O solution; 28.9mmols) was slowly dripped into a Et_2O solution of $(ClPNBu^t)_2$ (3.43g; 12.50 m mols) at 273K. The precipated LiCl was removed by filtration and the solvent removed from the filtrate to yield a white solid contaminated with LiCl. Attempted recrystallization from chloroform and hexane, and fractional distillation of the mixture did not yield a pure product.

<u>2Aiii With Methyl Magnesium iodide</u>

To an Et_2O solution of MeMgI (prepared from MeI (9.90g; 69.8 mmols) and Mg (1.70g; 69.9mmols)) was added, dropwise, to an Et_2O solution of $(ClPNBu^t)_2$ (9.21g; 33.5mmols), at 195K. After warming to room temperature, the precipitate was removed by filtration. The filtrate was fractional distilled to yield the product, $(Me_2PNBu^t)_2$, as a clear liquid which crystallised on cooling (bpt 335-339K at 0.8 mmHg ; 0.62g; 8%)

<u>Infra-red Data</u> (cm^{-1}nujol mull) 3420 (s) 3240(m) 2720(m) 2680(m) 2580(m) 2480(w) 2380(m) 2280(vw) 1900(vw) 1660(vs) 1600(m) 1400(m)1305(s) 1260(s) 1205(s) 1125(s) 1070(s) 1035(s) 1015(s) 990(msh) 945(m,sh) 925(m) 905(s) 890(s) 870(vs) 845(m) 810(m) 790(m) 765(m) 735(m) 720(m,sh) 690(m) 655(m) 595(w) 570(w) 520(m) 480(m,sh) 465(m,sh) 435(s)

<u>^{1}H.N.M.R. Data</u> (δ ppm; ref TMS:$CDCl_3$solution) 1.28(1)

<u>^{31}P.N.M.R. Data</u> (δ ppm; ref H_3PO_4 ; $CDCl_3$ solution)
-170.73

2Aiv With Dimethylamine

$HNMe_2$(9.00g;0.20mmols) was distilled onto an Et_2O solution of $(ClPNBu^t)_2$ (13.6g; 49.45 mmols), at 77K. After warming to ambient temperature, the precipitate was removed by filtration and solvent by distillation on the vacuum line. The white residue was redissolved in benzene and the solution heated at reflux for 20 hours. Fractional distillion yielded the product $(Me_2NPNBu^t)_2$ as a clear colourless liquid which crystallised on cooling, (bpt. 382-384K at 0.15mmHg; 107g;74%)

<u>Infra-red Data</u> (cm^{-1}; nujol and H.C.B. Mulls)
2956(s) 2815(s,sh) 2860(s) 2821(m) 2783(m) 1480(s,sh) 1470(s,Sh) 1455(s,br) 1425(m) 1400(m) 1385(s) 1359(s) 1273(s) 1240(s) 1210(vs,br) 1137(w) 1100(w) 1069(m) 1059(m) 1029(m) 998(s) 972(s) 961(s,sh) 923(w) 897(m) 866(s) 810(vw) 792(m) 728(vw) 688(m) 659(s) 645(m) 596(m) 552(vw) 488(w) 472(w) 417(w) 393(vw) 238(w) 210(w)

<u>^{1}H.N.M.R. Data</u> (δ ppm; ref TMS; $CDCl_3$solution) 1.19 (9) 2.63(3) 2.72(3)

<u>^{31}P.N.M.R. Data</u> (δ ppm; ref H_3PO_4; $CDCl_3$solution)
-94.8 (6) -182.7 (1)

<u>^{13}C.N.M.R. Data</u> (δ ppm; ref TMS; $CDCl_3$solution)

29.84 (4, Triplet J_{PNC} =5.88H_3) 3469(2,Doublet J_{PC} = 19.12H_3)

<u>Mass Spectrum</u> M^+292 (($Me_2NPBu^t)_2$ =292)

2B <u>Coordination Behaviour</u>

2Bi <u>Reaction of 1,3 di (tert-butyl) 2,4 dichloro 1,3,2,4-diazadiphosphetidine with titanium (IV) chloride</u>

A hexane solution (20cm^3) of $TiCl_4$ (0.70g; 3.6mmols) was added dropwise under a strict nitrogen atmosphere to a similar solution of $(ClPNBu^t)_2$ (1.20g; 4.20 mmols) contained in a 100cm^3 glass ampoule. A reaction occured almost instantly to give an orange solution and precipitate. The orange product (I) [$TiCl_4\{(ClPNBu^t)_2\}$] was immediately filtered and washed thoroughly with benzene and n-hexane to remove unchanged reactants and then pumped in vacuo for several hours (0.91g; 55%)

<u>Infra-red data</u> (cm^{-1}, nujol and H.C.B. Mulls) 2960(s) 2920(s) 2880(s) 2790(m) 2690(m) 2580(m) 2480(m) 2010(vw) 1625(m,br) 1590(s) 1495(w) 1470(m) 1400(m) 1370(s) 1310(m) 1290(m) 1255(m) 1175(s,br) 1040(s,br) 940(m) 915(m) 890(m) 900(w) 730(m) 720(m) 625(w) 560(w) 540(w) 435(s) 360-345(vs) 275(w)

<u>^{1}H.N.M.R. Data</u> (δ ppm; ref TMS; DMSO d^6solution) 1.27

<u>^{31}P.N.M.R. Data</u> (δ ppm; ref H_3PO_4; DMSO d^6 solution) 20(broa

<u>Chemical Analysis</u> (%) Found C:21.1, H:4.0, N:5.8, Cl;45.3

Calc'd for $C_8H_{18}N_2Cl_6P_2Ti$, C:20.7, H:3.9, N:6.0, Cl:45.8.

2Bii Reaction of 1,3 di(tert-butyl) 2,4bis (dimethylamino) 1,3,2,4 diazadiphosphetidine with titanium (IV) chloride

$TiCl_4$ (0.4cm^3; 3.64 mmols) in benzene (~10cm^3) was dripped into a benzene solution of $(Me_2NPNBu^t)_2$ (0.99g; 3.39 mmols). Immediate reaction occurs to give a dark green-brown solid and solution . Removal of solvent by distillation in vacuo followed by washing with hexane to remove unreacted starting materials afforded the product as an olive solid (II) (0.82g;50%)

Infra-red Data (cm^{-1}; nujol and HCB mulls) 3150(vw) 2950(m) 2910(m) 2850(w) 2800(w,sh) 1450(m,br) 1405(m) 1395(m) 1365(m) 1290(m) 1255(m) 1230(w) 1175(vs) 1090(m,sh) 1060(vs) 1040(s) 1025(vs) 1000(m,sh) 995(vs) 970(s) 915(w) 885(vs) 840(s) 815(m) 800(s) 815(w) 805(w) 775(w) 702(m) 685(vs) 671(m) 650(w) 608(m) 575(m) 545(w) 530(w) 510(w) 485(w) 420(vs,sh) 400(vs) 360(vs) 345(vs) 320(vs) 285(vs) 265(vs) 240(s)

^{1}H.N.M.R. Data (δppm; ref TMS; $CDCl_3$ solution) 1.38(6) 1.45(4) 2.74 (3) 2.91 (1) 297(2) 3.11(1)

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4;$CDCl_3$solution) -83.52 (3) -6.95 (4)

2Biii Reaction between 1.3 di (tert-butyl) 2, 4 dichloro-1,3,2,4 diazadiphosphetidine with norbornadienyl-molybdenum tetracarbonyl.

Benzene ($\sim 50cm^3$) was distilled onto a mixture of $[(nor\text{-}C_7H_8)Mo(CO)_4]$ (1.52g; 5.04 mmols) in vacuo at 77K. On warming to room temperature a blood red solution slowly developed. After a week the solution was concentrated and transferred to a chromatography column packed with Whatman CMII carboxymethyl cellulose and eluted with chloroform. A pale brown solid (III) was obtained by adding hexane to the concentrated chloroform solution.

Infra-red Data (cm^{-1}; nujol and H.C.B.mulls) 3200(m,sh) 3150(m,sh) 3100(m,sh) 2970(s) 2890(s) 2800(m) 2700(m) 2595(m) 2495(m) 2200(vw) 2080(m) 2030(m) 1975(s) 1940(vs,br) 1900(s,sh) 1710(w) 1695(w) 1590(w) 1495(s) 1465(m) 1455(m) 1440(w) 1430(w) 1390(s) 1368(s) 1363(s) 1320(m) 1285(s) 1250(s) 1185(s,br) 1150(s,br) 1130(s,br) 1050(vs,br) 1005(vs,br) 955(vs,br) 930(vs) 890(vs) 785(m) 750(m) 710(m) 615(m) 590(s) 570(s) 435(s) 410(w) 360(m) 335(m)

Chemical Analysis(%) Found C:35.06, H:5.98, N:4.30, Cl: 11.86, Mo:15.50 Calc'd for $C_{18}H_{32}N_2P_2Cl_2O_4Mo$; C: 37.91, H: 5.83, N: 4.91, Cl: 12.43, Mo: 16.82.

2B iv Reaction of 1,3 di(tert-butyl) 2,4 dichloro 1,3,2,4-diazadiphosphetidine and molybdenum hexa-carbonyl.

Dioxan was added to a mixture of $(ClPNBu^t)_2$ (3.63g; 13.20 mmols) and $Mo(CO)_6$ (3.54g; 13.41 mmols) the resulting solution was heated at reflux for 2½ hours.

then concentrated to ~5cm^3 and transferred to a chromatography packed with Whatman CMII carboxymethyl cellulose. A brown fraction was eluted with dichloromethane and a black one with T.H.F. Removal of solvent gave the major product as a brown solid (IV) and a trace amount of a black solid (V).

Brown solid (IV)

Infra-red Data (cm^{-1}; nujol and H.C.B. Mulls)

3200 (w,sh) 3110(m,sh) 3060(m,sh 2960(s) 2880(s) 2800(s) 2700(m) 2595(m) 2495(m) 2070(s) 2010(m,sh) 1995(s,sh) 1945(vs,br) 1915(ssh) 1770(vw,sh) 1730(w) 1700(vw,sh) 1685(vw,sh) 1510(m) 1475(w) 1460(w) 1445(w,sh) 1402(m) 1375(m) 1370(m) 1300(m) 1260(s) 1190(m) 1090(s) 1065(s) 1015(s) 930(vw) 900(w) 795(s) 720(vw) 620(w,sh) 600(m) 575(w) 450(w) 370(w)

^{1}H.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$ solution) 1.54

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; $CDCl_3$ solution) -8.09 (sl.br)

^{13}C.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$ solution) 234.2, -18.5- (sl,br)

Black Solid (V)

Infra-red Data (cm^{-1}; nujol and H.C.B. Mulls)

3040(m) 2975(s) 2900(m,sh) 2880(w,sh) 2790(w,sh) 1965(m) 1860(w) 1450(vw) 1400(w) 1370(w) 1300(w) 1250(m) 1225(m,sh) 1195(s) 1095(m) 1065(m) 1040(m) 1025(m) 930(m) 900(s) 880(m) 800(m) 720(w) 635(w,sh) 620(m) 545(w) 530(w) 490(m 430(m) 415(w,sh) 395(w) 320(w) 300(vw,sh)

2 Bv Reaction of 1.3 di(tert-butyl) 2.4 dichloro 1.3.2.4 diazadiphosphetidine with dimanganese decacarbonyl.

A mixture of $Mn_2(CO)_{10}$ (3.07g; 7.88 mmols) and $(ClPNBu^t)_2$ (2.09g; 7.60 mmols) was placed in a 250 cm^3 round bottomed flask fitted with a condenser and a nitrogen bubbler. p-Xylene ($\sim$100cm^3) was added and the initial yellow solution heated at reflux for ~15 mins. Filtration of the cooled solution, followed by recrystallisation of the solid material from T.H.F. gave the product, $[Mn(CO)\{(ClPNBu^t)_2\}_2]$ as a white solid(VI (0.85g; 31%). The filtrate was concentrated to ~5cm^3 and transferred to a chromatography column packed with 100-200 mesh Florisil.

Elution with n-hexane yielded a yellow solution shown by infra-red spectroscopy to be unreacted $Mn_2(CO)_{10}$. Further elution gave a dark brown solution which yielded a trace amount of a dark brown solid (A). Elution with T.H.F. gave two more brown fractions (B) and (C).

White solid (VI)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2995(s) 2975(s) 2950(s) 2905(s) 2890(s) 2795(vw) 2770(vw) 2310(vw) 2280(vw) 1920(m) 1870(vw) 1660(m) 1645(v,sh) 1465(m) 1455(m,sh) 1445(m,sh) 1375(m) 1350(m) 1320(w) 1300(w) 1270(m) 1255(w,sh) 1240(vw,sh) 1180(m) 1080(m,sh) 1060(m,sh) 1040(vs) 960(w) 925(s) 895(vs) 885(vs,sh) 805 (w) 730(w) 680(w) 465(vw,br)

^{1}H.N.M.R. Data (δ ppm; ref TMS; DMSO d^6 solution)

1.0 (broad)

Chemical Analysis (%) Found C: 34.5, H: 5.6, N: 8.9, Cl: 22.7, Calc'd for $C_{17}H_{36}N_4Cl_4OP_4Mn$, C: 32.2, H: 5.7, N: 8.8, Cl: 22.4

Dark Brown Solid (A)

Infra-red (cm^{-1}, CCl_4 solution) 2965 (m) 2930(m) 2880(w) 2100(w) 2080(s) 2060(s) 2040(m,sh) 2010(s,sh) 2000(vs) 1985(vs) 1970(vs) 1955(m,sh) 1936(m) 1925(msh) 1905(w) 1665(w) 1460(m) 1390(m) 1365(s) 1260(m) 1180(s) 1100(m 1035(m) 1015(m) 960(w) 870(m) 746(w,br) 675(vw) 650(s) 635(s) 495(w) 460(vw)

^{1}H.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$ solution)

1.57 (1, sl, br) 1.49(1) 1.33(1)

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; $CDCl_3$ solution)

- 103.56 (3) -129.00(1) -150.97(1) -186.6 (2)

Brown Solid (B)

Infra-red Data (cm^{-1} CCl_4 solution) 2980(s) 2940(s) 2870(m) 2080(m) 2010(s) 1995(s) 1985(s) 1973(s) 1940(m) 1660(vw) 1462(m) 1443(w) 1420(m) 1395(m) 1370(s) 1265(vs) 1225(w) 1190(s) 1100(vs) 1020(vs) 990(s) 905(m,sh) 870(s,br) 705(vw) 695(w) 665(w) 640(wO 625(vw,sh) 575(w) 510(w) 400(m) 360(w,sh)

^{1}H.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$ solution) 1.36

^{31}P.N.M.R. Data (δ pmm; ref H_3PO_4; $CDCl_3$ solution)

-71.27 (2) -98.56 (2) -128.96(3)

Brown solid (C)

Infra-red Data (cm^{-1}; CCl_4 solution) 2980 (vs) 2945(m) 2920(m) 2880(w) 2080(w) 2020(s) 1985(s) 1965(s,br) 1930(m,sh) 1465(w) 1400(w) 1370(m) 1270(m) 1255(w,sh) 1220(m) 1205(m) 1190(m) 1090(m,br) 1040(m) 1020(m) 900(w) 870(vw) 735(m) 660(w) 640(w) 570(vw) 500(vw) 435(vw) 395(vw)

^{1}H.N.M.R. Data (δ ppm;ref TMS; $CDCl_3$solution) 1.33(sl,br)

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; $CDCl_3$solution) -46.12(2) -55.17(2) -59.29(1) -71.37(6) -124.07(1) -141.09(1) -142.74(2) -144.39(2)

2Bvi Reaction of 1,3 di (tert-butyl) 2,4 dichloro 1,3,2,4-diazadiphosphetidine with diiron enneacarbonyl in a carbon monoxide atmosphere.

$Fe_2(CO)_9$ (1.34g; 3.68 mmols) and $(ClPNBu^t)_2$ (2.02g; 7.36 mmols) were placed in a 100 cm^3 glass ampoule and T.H.F. (~50 cm^3) distilled in under vacuum at 77K. The ampoule was filled with one atmosphere of carbon monoxide gas and sealed. On warming to R.T. a dark brown solution slowly developed. After 3 days, the solution was concentrated to ~5 cm^3 and transferred to a chromatography column packed with 100-200 mesh Florisil. Elution with T.H.F. yielded one major brown-red band, which gave a creamy brown solid (VII) on concentration and addition of n-hexane. Thorough washing with n-hexane and drying gave the pure product $[Fe(CO)_3\{(ClPNBu^t)_2\}]$ (0.61g; 20%).

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls)

2960(s) 2900(m) 2860(m) 2790(m) 2700(w) 2590(w)

2400(w) 2050(w) 2000(s) 1955(s) 1925(s) 1620(vw)

1500(w) 1455(w) 1390(w) 1365(w) 1295(w,sh) 1255(s)

1220(m,sh) 1200(s) 1130(w,sh) 1100(s) 1030(m,sh)

935(m) 920(s) 900(m) 800(w) 720(w) 625(m) 540(w)

450(m)

^{1}H.N.M.R. Data (δ ppm; ref TMS; DMSO d^6 solution) 1.33

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; DMSO d^6 solution) 10.46

Chemical Analysis (%) Found : 31.8, H: 4.5, N:6.9, Cl: 16.5 Calc'd for $C_{11}H_{18}Cl_2N_2O_3P_2Fe$ C: 31.8, H:4.4, N:6.7, Cl: 17.0.

2Bvii Reaction of 1,3 di(tert-butyl) 2,4 dichloro 1,3,2,4-diazadiphosphetidine with diiron enneacarbonyl under an inert atmosphere.

T.H.F. (~50 cm^3) was distilled onto a mixture of $Fe_2(CO)_9$ (1.35g; 3.70 mmols) and $(ClPNBu^t)_2$ (1.00g; 3.60 mmols) at 77K under vacuum, in a 100 cm^3 capacity glass ampoule. After degassing, the vessel was sealed under vacuum, and the contents allowed to slowly warm to room temperature. After 5 days, the red solution was concentrated and transferred to a chromatography column packed with 100-200 mesh Florisil. Elution with T.H.F. gave one brown-red major bond, which on concentration followed by addition of n-hexane gave the product, $[Fe_2(CO)_7\{(ClPNBu^t)_2\}]$ as a pale brown solid (VIII) (mpt, dec >470K; 0.71g 34%)

Infra-red Data (cm^{-1}; nujol and H.C.B.mulls)

2960(s) 2920(s) 2880(s,sh) 2790(m) 2730(m) 2690(m) 2580(m) 2480(m) 2360(vw) 2100(s) 2070(m,sh) 2047(s) 1990(s) 1960(s) 1925(s) 1715(w) 1500(m) 1460(s) 1440(s) 1395(s) 1368(s) 1285(s,sh) 1255(s,sh) 1245(vs) 1220(s) 1180(s,br) 1060(sbr) 1015(sbr) 975(m,br) 930(m,br) 875(s,br) 795(m) 715(m) 680(w) 675(w,sh) 638(m,sh) 615(m) 545(m,br) 440(m,br) 395(w,sh) 340(w) 280(vw)

^{1}H.N.M.R. Data (δ ppm; refTMS; $CDCl_3$ solution) 1.48

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; $CDCl_3$ solution)

17.08 (sl.br)

Chemical Analysis (%) Found C:30.6, H:2.9, N:5.0, Cl:12.2, MWT (Osmometric $CHCl_3$) : 576 Calc'd for $C_{15}H_{18}N_2Cl_2O_7P_2Fe_2$; C: 30.6, H:3.1, N:4.8, Cl:12.2, MWT: 583

2Bvii Reaction of 1.3 di (tert-butyl) 2.4 bis (dimethylamino)-1.3.2.4 diazadiphosphetidine with diiron enneacarbonyl.

T.H.F. (~50 cm^3) was distilled in vacuo onto a mixture of $Fe_2(CO)_9$ (0.99g; 2.72 mmols) and $(Me_2NPNBu^t)_2$ (0.80g ;2.74mmols) at 77K in a 100 cm^3 capacity glass ampoule. The reaction vessel was degassed and sealed under vacuum. On warming to R.T. a dark brown solution developed. After a week, the solvent was removed and the residue extracted with n-hexane to give a brown solution and an intractable oil. Concentration of the hexane solution followed by passage through a 100-200 mesh Florisil chromatography column gave two fractions (A, B).

Pale Brown Solid (A)

Infra-red Data (cm^{-1}; nujol mull and $CHCl_3$ solution)

3000(m) 2960(s) 2920(m) 2900(m) 2880(m) 2835(w) 2795(w) 2040(s) 1970(s) 1960(m,sh) 1935(vs) 1910(m,sh) 1390(w) 1365(m) 1275(w) 1255(m) 1235(w) 1215(w) 1195(m) 1170(w) 1095(m) 1055(m) 1035(m) 1010(s) 975(m) 965(m) 865(s) 800(s) 705(w) 395(w,br)

^{1}H.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$ solution)

1.32 (11) 2.57 (2) 2.80(3) 3.00 (2)

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; $CDCl_3$ solution)

-123.7 (4) -94.8 (5)

Brown Solid (B)

Infra-red Data (cm^{-1}; Nujol mull only) 2045 (m) 2038(m) 1967(m) 1935(vs) 1928(vs) 1898(m,sh) 1868 (s) 1290(w) 1270(m,sh) 1255(vs) 1195(s) 1170(w) 1085(vs) 1060(vs) 1025(vs) 1010(vs) 970(s) 920(w) 890(s) 860(w) 795(s) 735(w) 715(w) 690(w) 670(w) 615(s) 595(w,sh) 570(w) 525(w) 460(w) 385(w)

^{1}H.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$solution) 1.27(4) 1.33(3) 1.36(4) 1.42(7) 2.72(2) 2.77(3) 2.82(3) 2.87(3) 3.00(1)

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; $CDCl_3$ solution)

-15.04 (9) -11.20(5) -7.44 (5) -4.17(6) -1.80(9)

-7.11(3)

2Bxi Reaction of 1,3 di(tert-butyl) 2,4 dichloro 1,3,2,4 - diazadiphosphetidine and dicobalt octacarbonyl.

a) A hexane solution of $Co_2(CO)_8$ (1.30g; 3.80 mmols) was added to a similar solution of $(ClPNBu^t)_2$ (0.99g; 3.60 mmols) in a single ampoule which was then degassed and sealed under vacuum at 77K.On warming to R.T. a dark green-brown precipitate and solution formed. Extraction with hexane gave a green solid (IX) (0.32g) and a brown solution which yielded a brown solid (X) (0.80g). Both solids turned turquoise, (IX) rapidly on pumping and (X) slowly on storing sealed under vacuum.

Green Solid (IX)

Infra-red Data (cm^{-1}; nujol mull only) 2070(w) 2005(s) 1255(m) 1180(m) 1090(s) 1015(vs) 930(m) 900(m) 890(m) 800(m) 718(w) 540(w) 450(w) 385(m) 340(vw)

Turquoise solid from decomposition of green solid.

Infra—red Data (cm^{-1}; nujol and H.C.B. mulls) 2945(s) 2920(s) 2840(m) 2030(s) 1600(vw,br) 1455(w) 1400(w) 1370(m) 1255(s) 1230(w,sh) 1185(s) 1140(w) 1100(s) 1070(s) 1030(s) 975(vw) 940(m,sh) 920(m) 905(m) 880(s,sh) 875(s) 805(w) 720(m) 625(w) 545(m,sh) 530(m) 430(w)

Brown Solid (X)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls and $CHCl_3$ solution) 2955(m) 2920(m) 2870(w,sh) 2855(w) 2730(w) 2070(w) 2040(w) 2000(s) 1455(w) 1395(w) 1365(m) 1255(m) 1245(m,sh) 1220(w) 1185(m) 1080(s,br) 1035(s) 1005(s) 925(m) 850(s,br) 800(s) 720(vw) 645(w) 580(m) 545(m,sh) 525(s,sh) 510(s) 455(m) 420(m) 390(m) 345(w)

^{1}H.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$ solution) 1.30(sl,br

Turquoise solid from decomposition of brown solid.

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2950(m) 2920(m) 2845(w) 2070(s) 2000(s) 1965(m) 1925(m,br) 1605(bs) 1483(m) 1445(bs) 1365(w) 1260(w) 1240(w) 1215(m) 1200(w,sh) 1165(w) 1070(s) 1050(s) 1020(m) 885(w) 765(vs) 750(m) 700(vs) 690(vs) 660(m) 425(w) 345(m) 302(m)

b) Benzene was distilled on to a mixture of $Co_2(CO)_8$ (1.92g; 5.61 mmols) and $(ClPNBu^t)_2$ (1.69g; 6.15 mmols) under vacuum at 77K. After slow warming to R.T. the sealed reaction vessel was kept at 323K for a week. The solvent was removed from the brown solution and solid, the resulting brown product slowly decomposed to a turquoise solid. Infra-red and ^{1}H.N.M.R. data was identical as that obtained for the brown product (X) in (b)

2Bx. Reaction of 1,3 di(tert-butyl) 2,4 dichloro 1,3,2,4-diazadiphosphetidine with tetracarbonyl di-μ-chloro-dirhodium.

Hexane (~50 cm^3) was distilled in vacuo onto a mixture of $[Rh_2(CO)_4Cl_2]$ (0.93g; 2.40 mmols) and $(ClPNBu^t)_2$ (1.38g; 5.01 mmols) at 77K. After degassing, the ampoule was sealed and allowed to warm to ambient temperature when a slow reaction with bubbling occured. The pale lemon solid (XI) formed over several days, was removed by filtration, washed thoroughly with hexane and pumped dry. $[RhCl(CO)\{(ClPNBu^t)_2\}$ (1.71g;80%)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2970(s) 2960(s) 2950(s) 2920(s) 2860(m) 2730(m) 2020(s) 2005(w) 1455(s) 1395(m) 1370(s) 1245(w) 1225(w) 1180(w) 1080(w) 1045(s) 1030(s) 930(w) 885(s,sh) 865(s) 800(w) 720(w) 535(s) 455(m) 425(m) 392(s) 348(s) 272(s) 255(m)

^{1}H.N.M.R. Data (δ ppm; ref TMS; DMF d^7 solution) 1.65

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; DMF d^7 solution) -11.506(1) 6.257(1) After one month; -3.310(1) 3.633(1)

Chemical Analysis (%) found, C: 24.2, H:4.2, N:6.7, Cl:24.1 Calc'd for $C_9H_{18}Cl_3N_2OP_2Rh$; C:24.5, H:4.1, N:6.3, Cl:24.1.

DISCUSSION

2A. Halide replacement of 1,3 di(tert-butyl) 2,4 dichloro-1,3,2,4 diazadiphosphetidine.

With the hope of preparing more hydrolytically stable derivatives of the 1,3,2,4 diazadiphosphetidine rings, for possible investigations of their coordination behaviour, halide replacement reactions of $(ClPNBu^t)_2$ were undertaken:-

$$(ClPNBu^t)_2 + 2RM \longrightarrow (RPNBu^t)_2 + 2MCl$$

R= Me, Bu^n	M = Li
R = Me	M = MgI
R = NMe_2	M = H

During the course of this work several reports [155,162,167] appeared on the synthesis of these and other derivatives.

$(ClPNBu^t)_2$ is highly moisture sensitive and care is needed when handling. With $(RPNBu^t)_2$ (R = Bu^n, Me_2N) this problem was reduced, although prolonged contact with the atmosphere did cause decomposition. In the case of $(MePNBu^t)_2$ difficulty was experienced in purication and in obtaining high yields, this may have been due to air/moisture sensitivity. Addition of LiMe to $(ClPNBu^t)_2$ caused precipitation of a white solid, shown by its i.r. spectrum to be LiCl, indicating halide replacement had occurred. However a pure product could not be obtained by this method, inspite of repeated recrystallisation in a variety of solvents and attempted fractional distillation. $(MePNBu^t)_2$ was successfully prepared, as a white solid, by using MeMgI, but in very low yield.

This was the method used by Scherer and Schnabl [154], who also prepared it by cyclisation of $(Bu^tNH)_2PMe$ with $MePCl_2$. Our ^{31}P.N.M.R. data (Table 2.8) confirms replacement of both chlorines and is in agreement with that of Scherer and Schnabl. Infra-red data is given in Table 2.9.

Table 2.8 N.M.R. Data for $(XPNBu^t)_2$ (X= Cl, Me, Bu^n, NMe_2) compounds.

X	^{1}H.N.M.R. (δ ppm; refTMS)	^{31}P.N.M.R. (δ ppm; ref H_3PO_4)	^{13}C.N.M.R. (δ ppm; ref TMS)
Cl	1.41 (triplet;J_{PH}=IHz)	-207.67	30.32 (triplet; J_{PC}=6.1Hz)
Me	1.45 (Bu^t) 1.29 (Me) (doublet;J_{PH}=4.5Hz)	-170.73	
Bu^n	1.39(9) (Bu^t) 0.93(2), 1.22(1), 1.29(3), 1.32(2), 1.38(1)	-178.82	17.55, 15.01 (triplet;J_{PC}=4Hz) 10.53
Me_2N	1.19 (Bu^t) 2.68 (NMe_2) (doublet;J_{PH}=12.8Hz)	-182.7(1) -94.8(6)	29.84 (triplet J_{PC}=19.12Hz) 34.69 (doublet J_{PNC}=5.88Hz)

Table 2.9 Selected Infra-red Data for the 1,3,2,4 diazadiphosphetidines $(XPNBu^t)_2$ (X = Cl, MeBu^n and Me_2N) (cm^{-1})

$(ClPNBu^t)_2$	$(Me\ PNBu^t)_2$	$(Bu^nPNBu^t)_2$	$(Me_2NPNBu^t)_2$
2960 (s)		2960 (s)	2956 (s)
2925 (s)		2930 (s,sh)	2915 (s,sh)
2900 (m)		2900 (s,sh)	
2865 (m)		2870 (s)	2860 (s)
		2850 (m,sh)	2821 (m)
	2720 (m)	2710 (w)	2783 (m)
	2680 (m)		
	2580 (m)	2600 (w)	
1460 (s)		1460 (s)	1455 (s,br)
			1425 (m)
			1400 (m)
1395 (s)		1385 (m)	1385 (s)
1370 (s)		1375 (m)	1359 (s)
			1273 (s)
1240 (s)		1240 (s,sh)	1240 (s)
1200 (s,br)		1210 (s)	1210 (vs,br)
	1070 (s)		1058 (m)
1040 (s)	1035 (s)	1035 (s)	
1025 (s)	1015 (s)		1029 (m)
		1000 (s)	998 (s)

Table 2.9 Selected Infra-red Data for the 1.3.2.4 diaza-diphosphetidines $(XPNBu^t)_2$ (X = Cl.MeBu^n and Me$_2$N) (cm^{-1})

$(ClPNBu^t)_2$	$(Me\ PNBu^t)_2$	$(Bu^nPNBu^t)_2$	$(Me_2NPNBu^t)_2$
2960 (s)		2960 (s)	2956 (s)
2925 (s)		2930 (s,sh)	2915 (s,sh)
2900 (m)		2900 (s,sh)	
2865 (m)		2870 (s)	2860 (s)
		2850 (m,sh)	2821 (m)
	2720 (m)	2710 (w)	2783 (m)
	2680 (m)		
	2580 (m)	2600 (w)	
1460 (s)		1460 (s)	1455 (s,br)
			1425 (m)
			1400 (m)
1395 (s)		1385 (m)	1385 (s)
1370 (s)		1375 (m)	1359 (s)
			1273 (s)
1240 (s)		1240 (s,sh)	1240 (s)
1200 (s,br)		1210 (s)	1210 (vs,br)
	1070 (s)		1058 (m)
1040 (s)	1035 (s)	1035 (s)	
1025 (s)	1015 (s)		1029 (m)
		1000 (s)	998 (s)

Table 2.9 continued.

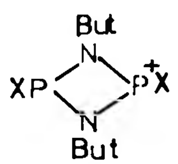
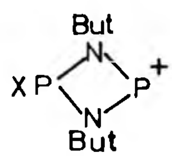
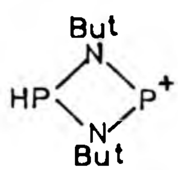
$(ClPNBu^t)_2$	$(MePNBu^t)_2$	$(Bu^nPNBu^t)_2$	$(Me_2NPNBu^t)_2$
		975 (s)	972 (s)
935 (s)	925 (m)	925 (m)	923 (w)
905 (s)	890 (s)	890 (s)	897 (m)
	870 (s)		866 (s)
	845 (m)	850 (s)	
	810 (m)	805 (w)	
	790 (m)	790 (m)	792 (m)
	765 (m)		
	735 (m)		
	690 (m)		688 (m)
	655 (m)		659 (s)
			645 (m)
		575 (m)	596 (m)
530 (m)			
490 (s)		480 (m)	
435 (m)	435 (s)		
395 (s)			

In contrast reaction with $LiBu^n$ proceeds smoothly to give $(Bu^nPNBu^t)_2$, in reasonable yield, as a straw coloured viscous liquid. One singlet at $-178.82\ \delta$ ppm in its ^{31}P.N.M.R. spectrum confirms replacement of both chlorines. Further evidence is provided by its mass spectrum which exhibits the parent ion at 318 ($(Bu^{n}PNBu^{t})_2$ = 318).

High yields of $(Me_2NPNBu^{t})_2$ were obtained provided excess $HNMe_2$ was used to remove the HCl evolved as amine hydrochloride. Replacement of both chlorides is confirmed by the mass spectrum, the highest $\frac{m}{e}$ value (292) corresponds to the parent ion $(Me_2NPNBu^{t})_2]^{+}$. Before heating the product in benzene, it exhibited two singlets (-182.7 and -94.8 δ ppm) with relative intensities 3:2 in its ^{31}P.N.M.R spectrum. On heating the intensity ratio of these peaks changes to 1:6. This is due to the formation of cis- and trans-isomers, the kinetically favoured isomer being converted to the thermally favoured isomer on heating. This has been studied by Bulloch et al,[161] who prepared a series of 2,4 diamino 1,3,2,4 diaza-diphosphetidines, many of which exhibited geometrical isomerism.

Replacement of chlorine for less electronegative groups result in the ^{31}P.N.M.R. resonances moving upfield, eg PCl_3: - 219, $PhPCl_2$: -162, Ph_2PCl: -81, Ph_3P: -6 δ ppm. This trend is reflected in the ^{31}P.N.M.R. spectra of the 1,3,2,4-diazadiphosphetidines prepared (Table 2.8). The mass spectra of the rings $(XPNBu^{t})_2$ (X =Cl, Bu^{n} and NMe_2) contain peaks corresponding to retention of the ring structure and to the monomer $(XPNBu^{t})$. The latter is increasingly stabilized in the series Cl $<$ Bu^{n} $<$ Me_2N (Table 2.10)

Table 2.10 Relative intensities of selected ions in the mass spectra of the 1,3,2,4 diazadiphosphetidine $(XPNBu^{t})_{2}$ - ($X = Cl$, Bu^{n} and $Me_{2}N$).

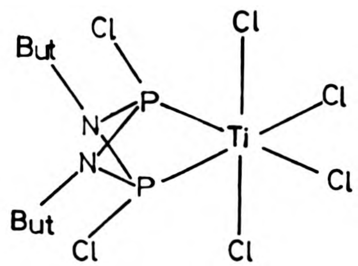
Ion	X=Cl	X= Bu^{n}	X= $Me_{2}N$
$(XP{=}NBu^{t})^{+}$	5	16	41
	33	6	38
	59	60	80
	36	30	18
$(P{=}NBu^{t})^{+}$	30	36	46
$(Bu^{t})^{+}$	100	100	100

2B Coordination behaviour of 1,3,2,4 diazadiphosphetidines.

The 1,3,2,4 diazadiphosphetidines are potential σ- donors to metal centres via the lone pairs of electrons of both the phosphorus and nitrogen atoms. Phosphorus donors are 'soft' Lewis bases and consequently are expected to preferentially form complexes with 'soft' Lewis acids. Whereas nitrogen donors are 'hard' Lewis bases and are expected to prefer 'hard' Lewis acids. 'Soft' Lewis acids tend to be metal ions of the heavier transition metals, and in lower oxidation states such as Ag(I), Pt(II), Hg(I), Fe(O), Mn(O). 'Hard' Lewis acids are generally metal ions of alkali metal, alkaline earth metals and lighter transitions metal in higher oxidation states such as Ti(IV), Cr (III), Mn(II), U(IV). Reactions of the 1,3,2,4 diazadiphosphetidines with various metal ions were studied in an attempt to obtain examples of both types of coordination behaviour.

2Bi Reaction of 1,3, di(tert-butyl) 2,4 dichloro 1,3,2,4 diazadiphosphetidine with titanium (IV) chloride.

$TiCl_4$ is a 'hard' Lewis acid and might be expected to promote coordination via the ring nitrogen atoms. Direct addition of $(ClPNBu^t)_2$ to $TiCl_4$ in hexane resulted in immediate precipitation of an extremely air-sensitive orange solid (I). One sharp methyl resonance (1.275 δppm), little shifted from that of the free ligand (1.41 δ ppm), in its ^{1}H.N.M.R. spectrum and one broadened signal (20 δ ppm), to highfield of the uncoordinated ligand (-207.9 δppm), in its ^{31}P.N.M.R. spectrum indicate bidentate phosphorous bonding. Analytical data confirms a 1:1 complex, formulated as the six-coordinate cis-complex $[TiCl_4\{(ClPNBu^t)_2\}]$ (A).



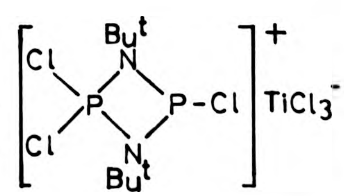
A

The low infra-red spectrum shows one strong, clearly multiple band in the 360-345 cm^{-1} region, consistent with a six-coordinate Ti (IV) species.[76] The band at 435 cm^{-1} is assigned to a (Ti-P) stretching mode; c.f. ν(Ti -P) 453 and 414 cm^{-1} for $[TiCl_4(Ph_2P(CH_2)_2PPh_2)]$.[183]

Phosphorus donation in this case is somewhat surprising, presumably the bulky Bu^t groups sterically hinder donation via the nitrogen lone pairs. Further the planarity of the ring nitrogens suggests delocalization within the ring reducing donor ability.

In contrast to amine complexes, phosphine complexes of Ti (IV) are rare. With the monodentate phosphines, PR_3, red complexes $[TiCl_4(PR_3)_2]$ (R=Et, Ph) and $[TiCl_4(PR_3)]$ (R=Me, Ph) have been prepared.[183-187] With the bidentate phosphines, $(R_2P(CH_2)_nPR_2)$ (R=Me,Et,n=2) and $(Et_2P(C_6H_4)PEt_2)$,

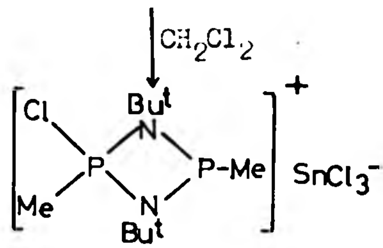
$TiCl_4$ gives 1:1 complexes.[187,188] With bis (diphenylphosphino) ethane (dpe), varying ratios of starting materials gave three products,[183,188] $[(TiCl_4(dpe)]$, $[(TiCl_4)_2(dpe)]$ and $[(TiCl_4)_3(dpe)_2]$. 1,2 bis (dimethylphosphino) benzene (dmb) gives an eight-coordinate complex $[TiCl_4(dmb)_2]$.[189] Allthese complexes were extremely moisture sensitive prohibiting extensive investigations so that comparative physical data is scarce. The general method of preparation was slow addition of a benzene solution of $TiCl_4$ to a benzene solution of the ligand in stiochiometric ratios. With our system, use of benzene (and most other common organic solvents) gave oily intractable products. Only with n-hexane was a solid product precipitated. The high instability in solution of the adduct made N.M.R. data collection difficult but this was minimized by collecting spectra of fresh solutions as rapidly as possible after preparation. This instability may be due, not only to hydrolysis, but also to rearrangement:-

$[TiCl_4\{(ClPNBu^t)_2\}]$ $\xrightarrow{\text{solution}}$ 

Allied work by Scherer and Schnable[135] has shown that reaction of 1,3,2,4 diazadiphosphetidines with $SnCl_4$, PCl_5 and $SbCl_5$ leads to formation of 1,3,2,4 diazadiphosphoniumphosphetidines and the anions $SnCl_3^-$, Cl^- and $SbCl_4^-$

respectively. With $SnCl_4$, a 1:1 adduct was formed which decomposed in CH_2Cl_2 :-

$$(MePNBu^t)_2 + SnCl_4 \longrightarrow [SnCl_4\{(MePNBu^t)_2\}]$$



This 1:1 $SnCl_4$ adduct was proposed to have the ring coordinated via the two nitrogen atoms since:-

a) $\delta C\underline{H}_3P$ occurs in the range expected for Me bonded to tri-coordinate phosphorus.

b) $^2J_{PH}$ was found to be less than that obtained for the four-coordinate phosphorus atom in the 1,3,2,4-diazadiphosphoniumphosphetidines.

c) Blocking the phosphorus atoms by using the dithio derivative still gave a 1:1 adduct.

$$(Me(S)PNBu^t)_2 + SnCl_4 \longrightarrow [SnCl_4\{(Me(S)PNBu^t)_2\}]$$

In the latter case coordination via the sulphur atoms is deemed just as likely and without ^{31}P.N.M.R. evidence their formulation can only be speculative. In the light of our results with $TiCl_4$ and bearing in mind the similar behaviour exhibited by $TiCl_4$ and $SnCl_4$ (both are considered to be 'hard' Lewis acids; similar ionic radii, $Sn^{4+} = 0.71$, $Ti^{4+} = 0.68$Å and octahedral covalent radii, Sn(IV) = 1.45, Ti(IV) = 1.36Å) it seems more likely that the $(PN)_2$ ring will function as a bidentate phosphorus donors in these cases as well.

2Bii Reaction of 1,3 di(tert-butyl) 2,4 bis (dimethylamino)-1,3,2,4 diazadiphosphetidine with titanium (IV) chloride.

The ^{31}P.N.M.R. spectrum of the free ligand shows the existence of cis- and trans- forms in solution, with two singlets at -182.7 and -94.8 δppm, relative intensities 1:6 The olive green, very air-sensitive $TiCl_4$ complex (II) similarly exhibited two sharp singlets in its ^{31}P.N.M.R. spectrum (Fig 2.6) at -83.53 and - 6.95 δppm, relative intensities 3:4. Donation via one phosphorus and one nitrogen atom is thus ruled out since a pair of doublets resulting from ^{31}P - ^{31}P coupling of the inequivalent nuclei are not observed. The large upfield shifts recorded suggest phosphorus rather than nitrogen donation. This is supported by little change in the chemical shifts of the n-Bu^t and N-Me protons.

The low infra-red spectrum of the product contains absorptions at 360,345,320, and 285 cm^{-1} characteristic of octahedral (Ti-Cl) stretching modes.[76] Bands at 420 and 400 cm^{-1} are also observed and are tentatively assigned to (Ti-P) stretching vibrations. For the cis-isomer, a structure analogous to that proposed for $[TiCl_4\{(ClPNBu^t)_2\}]$ may be envisaged (B). However for the trans-isomer the stereochemistry of the ring makes a similar arrangement unlikely and a polymeric complex with bridging rings seems more plausible (C).

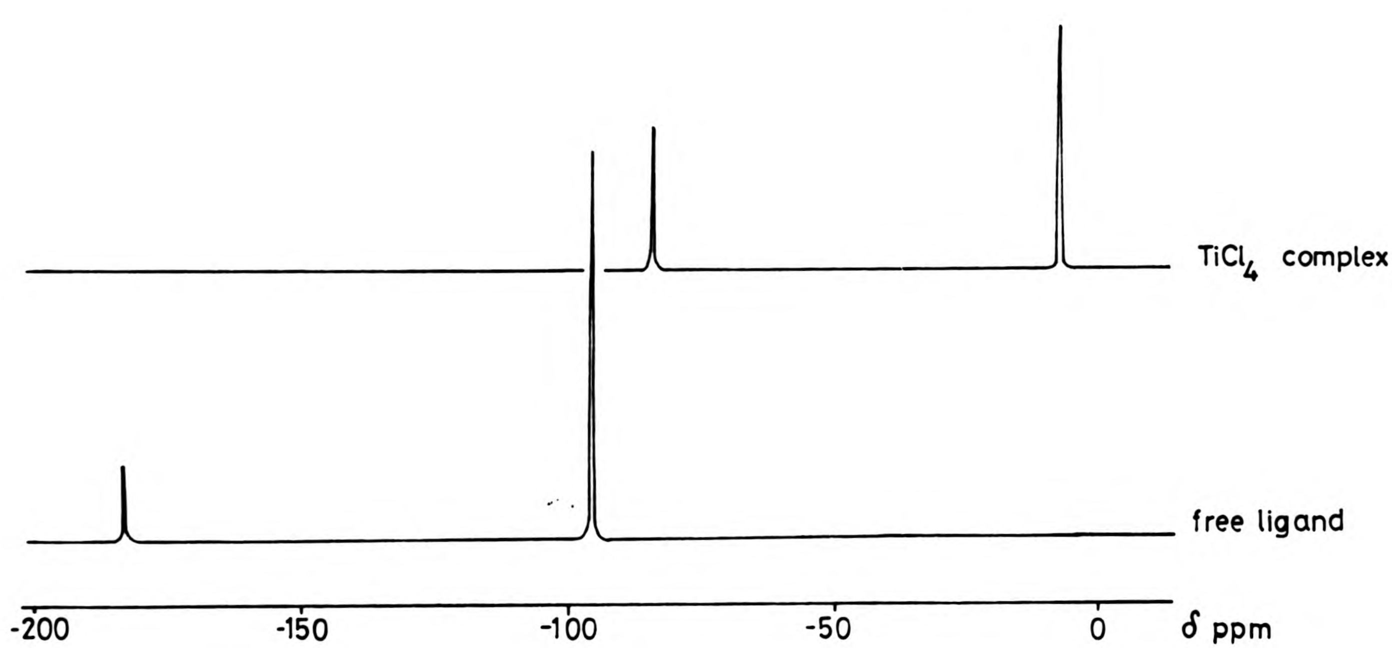
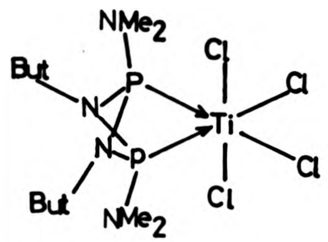
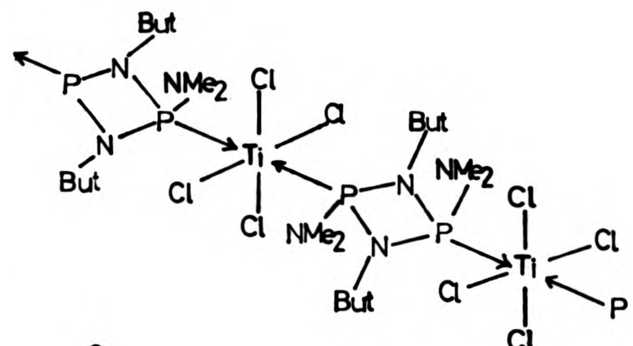


Fig. 2.6 Schematic diagram of ^{31}PNMR of $[(Me_2N)PNBu^t]_2$ and its $TiCl_4$ complex.



B

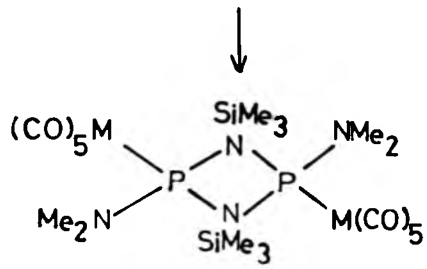


C

2Biii Reaction between 1.3 di(tert-butyl) 2.4 dichloro-1.3.2.4 diazadiphosphetidine and molybdenum carbonyl complexes.

During our initial studies of the coordinating ability 1,3,2,4 diazadiphosphetidines, the reactions of $Mo(CO)_6$ and $[(nor\text{-}C_7H_8)\ Mo(CO)_4]$ were the first we attempted. No consistent or obvious result, however, could be obtained. In the middle of our studies Zeiss and Feldt[190] reported the synthesis of molybdenum and chromium complexes in which $(Me_2NPNSiMe_3)_2$ acts as a bidentate donor to two metal centres:-

$$2\ [(MeCN)\ M(CO)_5] + (Me_2NPNSiMe_3)_2$$



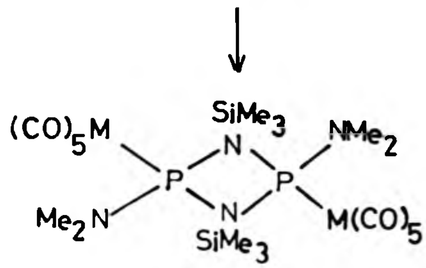
(M=Mo, Cr)

Addition of $(ClPNBu^t)_2$ to $[(nor\text{-}C_7H_8)\ Mo(CO)_4]$ gave a red solution from which a pale brown solid (III) could be precipitated with n-hexane. The ν(C-O) region of the i.r. spectrum of the product contains four bands (2080(m) 2030(m) 1975(s) 1940(vs,br) cm^{-1}) consistent with cis-$[Mo(CO)_4\{(ClPNBu^t)_2\}]$.[63] The frequencies observed are comparable to those of analogous acyclic diphosphine derivatives (Table 2.11)

Table 2.11 Infra-red data for some $[Mo(CO)_4(L\text{-}L)]$ complexes.

L-L	ν(C-O) (cm^{-1})				Ref
$Ph_2P(CH_2)_2PPh_2$	2020(s)	1919(s)	1907(vs)	1881(s)	189
$Ph_2PCH_2PPh_2$	2020(s)	1920(sh)	1907(vs)	1879(s)	189
$MePhP(CH_2)_2PPh_2$	2025(m)	1930(m)	1904(s)	1901(s)	190
$EtPhP(CH_2)_2PPh_2$	2020(m)	1927(m)	1908(s)	1901(s)	190
$(PPh_2)_2NMe$	2025	1933	1912	1907	191

$$2\ [(MeCN)\ M(CO)_5] + (Me_2NPNSiMe_3)_2$$



(M=Mo, Cr)

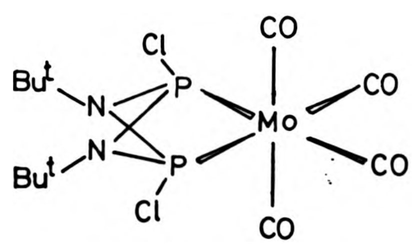
Addition of $(ClPNBu^t)_2$ to $[(nor\text{-}C_7H_8)\ Mo(CO)_4]$ gave a red solution from which a pale brown solid (III) could be precipitated with n-hexane. The ν(C-O) region of the i.r. spectrum of the product contains four bands (2080(m) 2030(m) 1975(s) 1940(vs,br) cm^{-1}) consistent with cis-$[Mo(CO)_4\{(ClPNBu^t)_2\}]$.[63] The frequencies observed are comparable to those of analogous acyclic diphosphine derivatives (Table 2.11)

<u>Table 2.11 Infra-red data for some $[Mo(CO)_4(L\text{-}L)]$ complexes.</u>

L-L	ν(C-O) (cm^{-1})				Ref
$Ph_2P(CH_2)_2PPh_2$	2020(s)	1919(s)	1907(vs)	1881(s)	189
$Ph_2PCH_2PPh_2$	2020(s)	1920(sh)	1907(vs)	1879(s)	189
$MePhP(CH_2)_2PPh_2$	2025(m)	1930(m)	1904(s)	1901(s)	190
$EtPhP(CH_2)_2PPh_2$	2020(m)	1927(m)	1908(s)	1901(s)	190
$(PPh_2)_2NMe$	2025	1933	1912	1907	191

The shoulder observed ($1900cm^{-1}$) in our complex may be due to the slight lowering of the symmetry from the regular octahedral arrangement in the solid state necessitated by the steric constraints of the ligand as found in $[Mo(CO)_4\{(PH_2P)_2CH_2\}]$ [194].

Analytical data is consistent with $[Mo(CO)_4\{(ClPNBu^t)_2\}]$-.n-hexane; ie n-hexane present as solvent of crystallisation. Unfortunately no reliable ^{1}H or ^{31}P.N.M.R. data could be obtained to confirm this formulation. On the basis of our limited data and the pattern of coordination behaviour of these rings revealed by our study, the structure proposed involves the $(P-N)_2$ ring as a cis-bidentate phosphorus donor. (D)



D

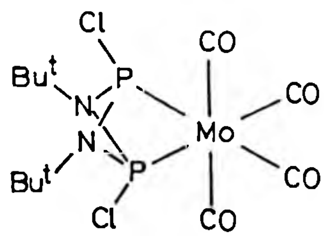
2Biv. Direct use of $Mo(CO)_6$ yields two products largely a brown solid (IV) and trace amounts of a black solid (V).

The brown solid (IV) exhibits a single resonance in its ^{31}P.N.M.R. spectrum at -8.09 δppm, the large upfield shift from that observed for the free ligand indicating donation via both phosphorus atoms. The ^{13}C.N.M.R. spectrum contains two resonances (234.2 -18.2δppm). (NB. the convention for ^{13}C.N.M.R. spectra is the reverse of that for ^{31}P.N.M.R. so that + values occur to low field of the TMS reference signal.) For molybdenum carbonyl complexes, ^{13}CO shemical shifts have been observed at 200 δ ppm.[193] This is in agreement with our intrepretation that , for our complex, the signal at 234.2 δ ppm is due to $^{13}\underline{C}O$ and that at -18.2 δ ppm to $^{13}(\underline{C}H_3)_3C$ (cf the value of 30.32 δ ppm for the free ligand). A resonance due to $^{13}\underline{C}(CH_3)_3$ is not observed, not surprisingly as the lack of directly bound protons means there is no nuclear overhauser enhancement. The resonances show the expected downfield shift from the parent carbonyl; compare with data for similar molybdenum complexes (Table 2.12).

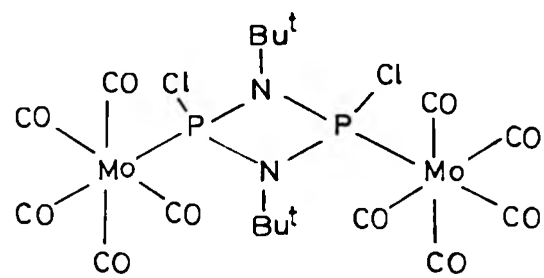
<u>Table 2.12 ^{13}C.N.M.R. data for molybdenum hexacarbonyl and selected derivatives</u>.

Complex	δ ^{13}CO (δ ppm; ref TMS) cis	trans
$Mo(CO)_6$	202.2	
$[Mo(CO)_5\{P(OMe)_3\}]$	206.4	209.2
$[Mo(CO)_5(PPh_3)]$	206.5	211.0
trans-$[Mo(CO)_4\{P(OMe)_3\}_2]$	210.3	
cis-$[Mo(CO)_4(Ph_2PCH_2)_2]$	210.6	218.5

From the data available it is not possible to discern between a cis-bidentate coordination to a $Mo(CO)_4$ unit (<u>E</u>) or a bridging mode to two $Mo(CO)_5$ units (F).



E



F

The black solid (V) shows a much simpler ν(CO) stretching pattern (1965(m) 1860 (w) cm^{-1}) than the other products. This could be due to coordination of two $(P-N)_2$ rings, giving $[Mo(CO)_2\{(ClPNBu^t)_2\}_2]$- the cis-isomer of which is predicted to give two i.r. active (C-O) stretching bands (A_1 + B_1).[63] However the expulsion of carbonyl groups by tervalent phosphorus compounds proceeds stepwise with increasing difficulty, since as the carbonyl groups are replaced the strength of the remaining M-C bonds increases due to enhanced (M-C)π bonding resulting from substitution by ligands which are better σ-donors but poorer π-acceptors than CO. Tertiary phosphines readily replace two carbonyls, the more electronegative phosphines may replace a third and in some cases a fourth carbonyl group (Table 2.13).[191]

Table 2.13 Some phosphine derivatives of Molybdenum carbonyls.

Compound	Reaction Conditions
$[Mo(CO)_4(Et_2PCH_2)_2]$	423-433K for 6 hours
$[Mo(CO)_4(Ph_2PCH_2)_2]$ (a)	423K for 5 hours followed by 443K for 4 hours.
$[Mo(CO)_3(PhP\{(CH_2)_2PPh_2\}_2)]$	423K for 15 hours.
cis-$[Mo(CO)_2(Ph_2PCH_2)_2]$	Mixture of (a) and xs diphosphine 583-593K for 60 hours.

Dicarbonyl derivatives have only been prepared under forcing conditions and thus this interpretation is only speculative.

2Bv Reaction of 1.3 di(tert-butyl) 2.4 dichloro 1.3.2.4 diazadiphosphetidine with dimanganese decacarbonyl.

The interaction of acyclic diphosphines with $Mn_2(CO)_{10}$ has been shown to give a wide variety of products under varying conditions[196-199] (Table 2.14).

Not surprisingly the reaction of $Mn_2(CO)_{10}$ and $(ClPNBu^t)_2$ gave a mixture of products and only one of these $[Mn(CO)-\{(ClPNBu^t)_2\}_2]$ was positively identified. A variety of solvents, typically benzene, hexane, T.H.F. and p-xylene, and variable stiochiometry (1:1,1:2,1:xs) were tried (see experimental section for typical example). In all cases mixtures were obtained which proved very difficult to separate. Although column chromatography gave some degree of separation, the resultant fractions were impure mixture as confirmed by N.M.R.

Table 2.14 Various products from the reaction of acyclic diphosphines with $Mn_2(CO)_{10}$

Ligand L	$Mn_2(CO)_{10}$: L	Conditions	Product Type
dpe*	1:5	Irradiated 2 hours in benzene	$[Mn(CO)L_2]$
dpe	1:xs	Reflux in dimethoxy-ethane	$[Mn(CO)_2L_2]$. $[Mn(CO)_5]$
dpe	1:1	Irradiated 3 hours in benzene	$[Mn(CO)_3L]$
dpm+	1:2	Refluxed 2 hours in n-decane	$[HMn(CO)_3L]$
dpm	1:2	Refluxed 4 hours in p-xylene	$[Mn_2(CO)_5L_2]$
dpm	1:2	Refluxed 24 hours in benzene	$[Mn_2(CO)_6L_2]$
dpm dpe	1:1	Refluxed 8 hours in benzene	$[Mn_2(CO)_8L]$

*dpe = 1,2 bis (diphenylphosphino) ethane

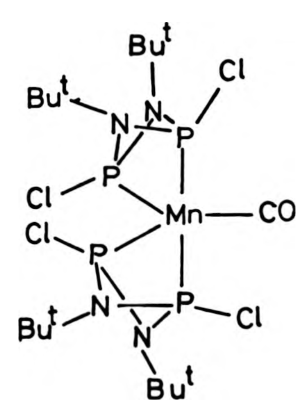
+dpm = 1,2 bis (diphenylphosphino) methane

The white product (VI) $[Mn(CO)\{(ClPNBu^t)_2\}_2]$ precipitated from p-xylene and was purified by repeated recrystallisation from T.H.F.

The tendency for transitionmetal complexes in low oxidation states to form stable covalent bonds with hydrogen is so great that hydride containing metal carbonyls have sometimes been formed unexpectedly, hydrogen having been abstracted from the solvent or the ligand, eg:-

$$\tfrac{1}{2}Mn_2(CO)_{10} + 2Ph_3P \xrightarrow[\text{p-xylene}]{\text{reflux}} [HMn(CO)_3(Ph_3P)_2]$$

realistically there can be no analytical distinction between $[Mn(CO)\{(ClPNBu^t)_2\}_2]$ and the hydride $[HMn(CO)\{(ClPNBu^t)_2\}_2]$ and it is possible that our product may have the latter formulation. However no spectral evidence - neither an Mn-H resonance in the ^{1}H.N.M.R. nor a ν(Mn-H) stretching mode in the infra-red - can be located. The ν(C-O) and ν(M-H) region of the i.r. spectrum contains one medium band (1920cm^{-1}) assigned to the (C-O) stretching mode of the single carbonyl group, there is some evidence for a second band (1870cm^{-1}) but it is extremely weak. The C$\underline{H}_3$ proton resonance appears as a very broad signal poorly resolved at 1.0 δ ppm supporting the proposed five-coordinate paramagnetic structure (G).



G

Although reliable ^{31}P.N.M.R. data could not be obtained, by analogy with the other complexes obtained it is proposed that the $(P\text{-}N)_2$ ring acts as a bidentate phosphorus donor in this case as well. The i.r. band at 465 cm^{-1} is tentatively assigned to ν(Mn-P) stretching mode.

<u>2Bvi Reaction of 1.3. di(tert-butyl) 2.4 dichloro 1.3.2.4 diazadiphosphetidine with diiron enneacarbonyl</u>.

Cotton et al[200] have demonstrated that when $Fe_2(CO)_9$ is dissolved in T.H.F. the resulting "solution" is very reactive. The true nature of this "solution" has not been elucidated but is thought to contain species such as $[Fe(CO)_4.THF]$ when a CO atmosphere is maintained.

$$Fe_2(CO)_9 + THF \xrightarrow[300K]{1\ atmos.\ CO} Fe(CO)_5 + [Fe(CO)_4.THF]$$

$$[Fe(CO)_4.THF] + L \longrightarrow [Fe(CO)_4L] + THF$$

The reaction system is obviously more complex than implied by these equations, since without a CO pressure substitution products of $Fe_2(CO)_9$ itself can be obtained. Depending on reaction conditions, varying relative amounts of three main types of product have been isolated. With a partial pressure of CO the main product is a mononuclear species. Whereas with an inert gas flush dinuclear species are primarily formed. In both cases small quantities of polynuclear species can be obtained (Table 2.15)

In many cases addition of N,O,P or S donor ligands gives metal complexes otherwise difficult to isolate. For example in the presence of pyridine or pyrazine, with a CO atmosphere the amine derivatives $[Fe(CO)_4L]$ (L=py, pyr) were isolated, [202] the

Table 2.15 Some products obtained by reacting diiron enneacarbonyl with various ligands in THF.

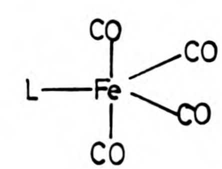
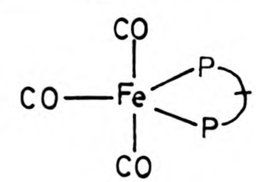
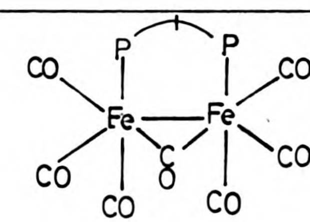
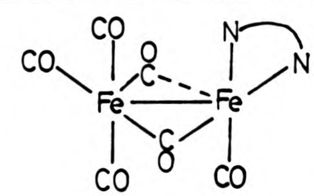
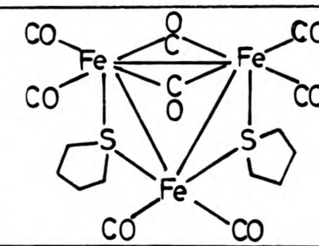
Ligand	Reaction conditions	Products		Ref.
C_5H_5N	With CO	$(C_5H_5N)\ Fe(CO)_4$		201
$C_4H_{14}N_2$	With CO	$(C_4H_{14}N_2)\ Fe(CO)_4$		201 209
$C_{12}H_{18}$	With CO	$(C_{12}H_{18})\ Fe(CO)_4$		210
$(Ph_2P)_2CH_2$	With CO	$(Ph_2P)_2CH_2\ Fe(CO)_3$		206 208
$(Ph_2P)_2CH_2$	Inert atmosphere	$(Ph_2P)_2CH_2\ Fe_2(CO)_7$		207 211

Table 2.15. continued.

Ligand	Reaction conditions	Products		Ref.
$C_{10}H_8N_2$	Inert atmosphere	$[(C_{10}H_8N_2)\ Fe_2(CO)_7]$		205
C_4H_8S		$[(C_4H_8S)_2\ Fe_3(CO)_8]$		204

first of the class $[Fe(CO)_4(Amine)]$ (except for Am=NH_3, which has been prepared by reaction of hydroxylamine-o-sulphonate ion with the $[FeH(CO)_4]^-$ anion[202]. Under similar conditions but without a CO atmosphere $Fe_2(CO)_9$ reacts with 2,2′ bipyridyl to afford a binuclear complex, $[Fe_2(CO)_7(bipy)]$. This compound is of interest since it contains one highly unsymmetrical bridging carbonyl group, defined by Cotton as a "semi-bridging carbonyl group" (S.B.C.O). A crystal structure determination of this complex has shown that the 2,2′ bipyridyl group is bound to one metal only. Since the nitrogen base rings are excellent σ-donors but very poor π-acceptors, there is considerable build up of electron density on this iron centre. One effect of this is to distort the bridging CO group (Fig 2.7).

In the reaction of $(ClPNBu^t)_2$ with $Fe_2(CO)_9$ in T.H.F., under an atmosphere of CO gas the expected mononuclear complex, $[Fe(CO)_3\{(ClPNBu^t)_2\}]$ was obtained. In the degassed system the binuclear complex $[Fe_2(CO)_7\{(ClPNBu^t)_2\}]$ was formed preferentially. Trace amounts of a third product were obtained in both experiments, presumably corresponding to Cotton's polynuclear species but could not be fully characterized.

The creamy brown mononuclear product (VII) shows three major i.r. bands in the ν(CO) region, (2000(s) 1955(s) 1925(s) cm^{-1}) with an additional weak band at 2050 cm^{-1}, consistent with a five-coordinate geometry [63] (except a trans-trigonal bipyramid The equivalent Bu^t groups give one proton resonance (1.33δppm), little altered from that of the free ligand. In contrast the ^{31}P.N.M.R. spectrum contains a singlet at much higher field

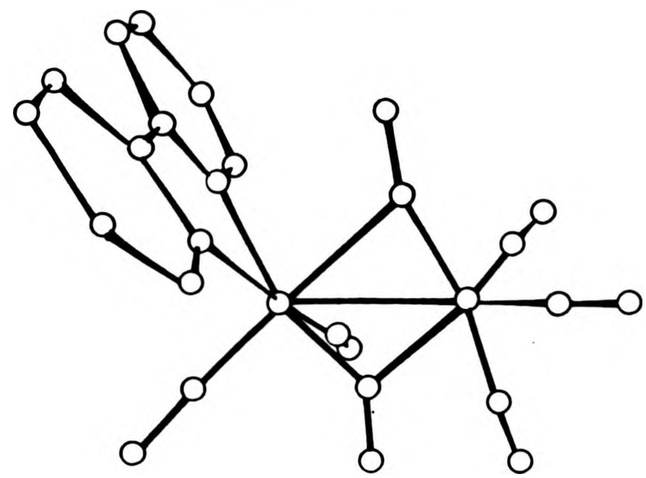


Fig. 2.7 Structure of [$Fe_2(CO)_7$bipy].

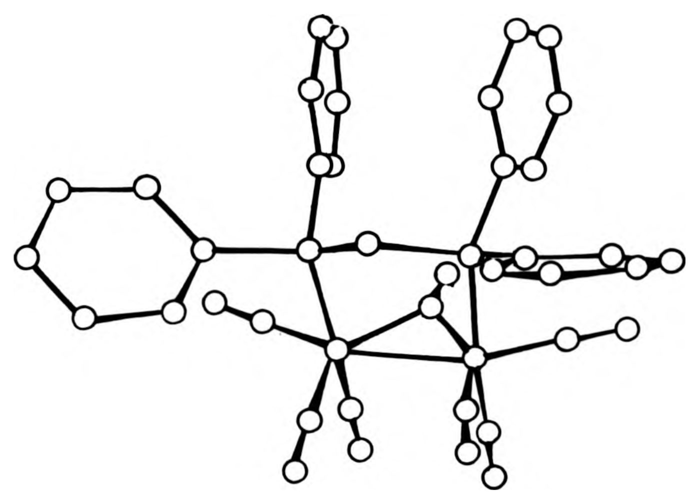
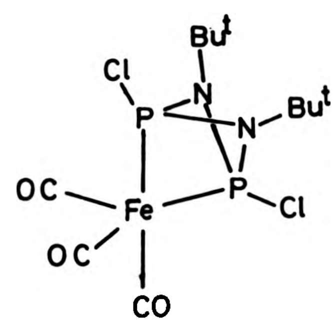


Fig. 2.8 Structure of [$Fe_2(CO)_7Ph_2PCH_2PPh_2$].

(10.46 δ ppm) than the uncoordinated ligand. Bidentate phosphorus coordination is thus inferred.

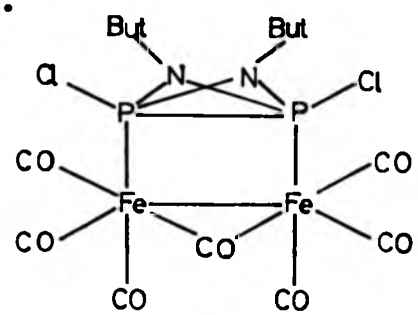
The diphosphine analog $[Fe(CO)_3\{(Ph_2P)_2CH_2\}]$ is a fluxional molecule whose actual structure lies between the idealized trigonal bipyramidal ~ rectangular pyramid geometries with all three carbonyl groups non-equivalent. A similar structure is proposed for $[Fe(CO)_3\{(ClPNBu^t)_2\}]$ with the $(P\text{-}N)_2$ as a chelating bidentate phosphorus donor (H).



H

Unfortunately a low temperature N.M.R. study could not be undertaken to investigate any fluxional characteristics for this molecule due to its very low solubility in suitable solvents.

2Bvii With reference to $[Fe_2(CO)_7(bipy)]$ and $[Fe_2(CO)_7(Ph_2P)_2CH_2$ (Fig. 2.8) it is evident that both bridging and chelating forms are possible for the binuclear product (VIII). In the latter case a semi-bridging carbonyl group would be expected and the absence of a ν(C-O) band at 1850cm^{-1} suggests this unlikely. The complex exhibits six bands (2100(s) 2047(s) 1991(s) 1960(s) 1925(s) cm^{-1}) in the ν(C-O) terminal stretching infra-red region and one band (1715(w) cm^{-1}) in the ν(C-O) bridging region. This is in accordance with that predicted for the bridging form. ^{31}P.N.M.R. evidence indicates bidentate phosphorus donation (singlet; 17.08 δ ppm), and the proposed structure contains the ligand bridging two iron atoms (J).



J

2Bviii Reaction between 1,3 di(tert-butyl) 2,4 bis (dimethylamino) 1,3,2,4 diazadiphosphetidine and diiron enneacarbonyl.

Reaction $(Me_2NPNBu^t)_2$ with $Fe_2(CO)_9$ in a degassed system resulted in the formation of inseparable mixtures of products. Column chromatography of the mixture gave two fractions, the ^{31}P.N.M.R. of which indicated that each contains more than one compound (Fig 2.9). The first appears to contain one isomer of the unreacted ligand (-94.6 δ ppm) and another species with equivalent phosphorus atom (-123.7 δ ppm). The other fraction gives a much more complex ^{31}P.N.M.R. spectrum. It appears that a variety of products are present, not surprisingly since the exocyclic nitrogen atoms may also coordinate and the

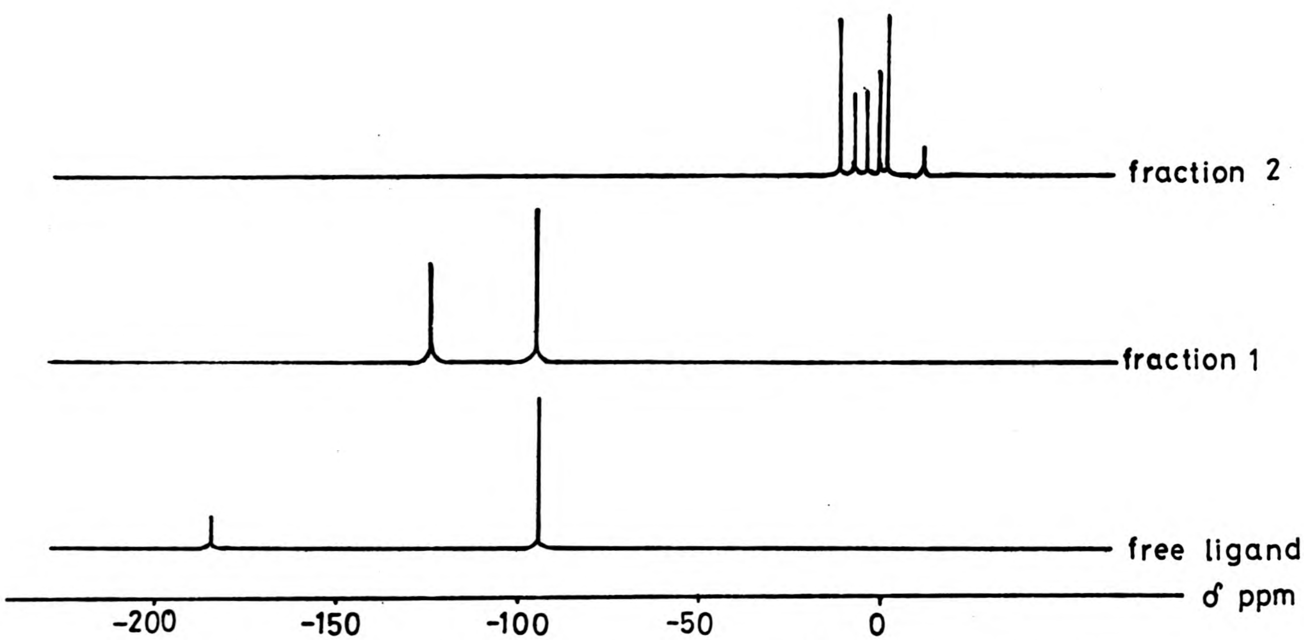


Fig. 2.9 Schematic diagram of the ^{31}P.N.M.R. spectra of $[(Me_2N)PNBu^t]_2$ and its iron carbonyl complexes.

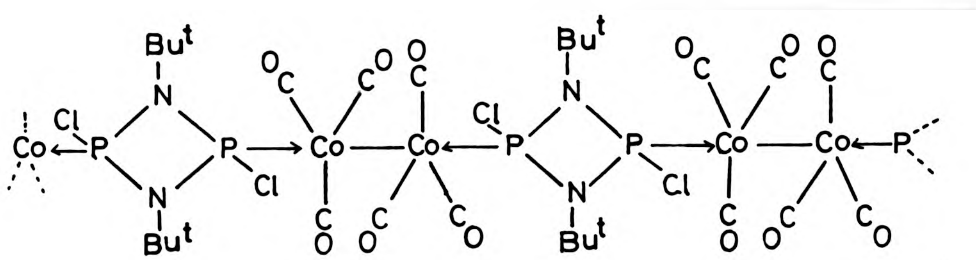
stereochemistry of the two isomers may dictate formation of different complexes. In consequence, inspite of attempted separation by various methods, no single product could be isolated and characterized.

2Bix Reaction of 1,3 di (tert-butyl) 2,4 dichloro 1,3,2,4-diazadiphosphetidine with dicobalt octacarbonyl.

Various complexes have been isolated from the reaction of $Co_2(CO)_8$ and diphosphines, depending on the reaction conditions. At low temperatures, in both polar and non-polar solvents, ionic complexes, eg:- $[Co_2(CO)_4(dpe)_3]^{2+}$–$2[Co(CO)_4]^-$ and $[Co(CO)_3(dpb)]^+[Co(CO)_4]^-$ (dpe= $(Ph_2P)_2(CH_2)_2$ and dpb= $(Ph_2P)_2(CH_2)_4$), are formed. Higher temperatures favour covalent complexes such as $[Co_2(CO)_4(dpe)_2]$ and $[Co_2(CO)_6(dpb)]$.[198,212-215] Both types of complex tend to be unstable, decomposing on storage in the solid state. On the basis of i.r. data, various isomers may be proposed for each of these examples, those with bridging carbonyl groups being considered as derivatives of the bridged form of $Co_2(CO)_8$.

Reaction of $(ClPNBu^t)_2$ and $Co_2(CO)_8$ gave two products. At ambient temperature a mixture of a dark brown, hexane soluble, product (X) and an insoluble green solid (IX) formed. At 323K only a dark brown solid, identical to the former, was obtained. The green product was unstable at R.T., decomposing on pumping to remove solvent. Consequently only limited data could be collected. Infra-red evidence confirms the presence of CO groups (2070(w), 2005(s) cm^{-1}) but, although analogous systems might suggest this was an ionic complex, no band due to the anion $[Co(CO)_4]^-$ (1885 cm^{-1})[212] could be located.

The brown product (X) exhibits three main i.r. bands in the ν(C-O) $_{terminal}$ stretching region (2070(w) 2040(w) 2000(vs) cm^{-1}). No bands assignable to bridging CO groups were observed. A possible structure, consistent with this data is that a ligand bridged polymer (K). (cf the structure proposed for $[Co_2(CO)_6(dpb)]$ [212]).



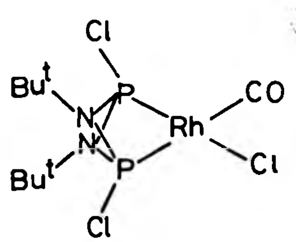
K

Such a structure would give rise to one carbonyl absorption.[63] Phosphorus donation is tentativively proposed since the ^{1}H.N.M.R. spectrum shows a slightly broad singlet (1.30 δ pmm) little shifted from that of the free ligand. This complex is also unstable at R.T. over long periods, decomposing slowly to a turquoise solid, preventing chemical analysis.

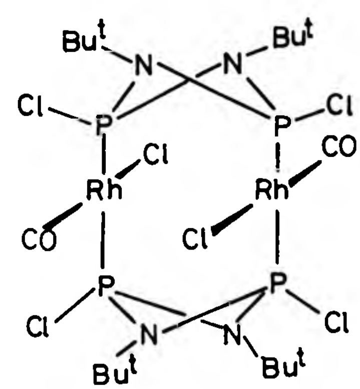
2Px. Reaction of 1.3 di(tert-butyl) 2.4 dichloro 1.3.2.4 diazadiphoshetidine with tetracarbonyl di-μ- chloro dirhodium.

Treatment of $Rh_2Cl_2(CO)_4$ with $(ClPNBu^t)_2$ in hexane gave a yellow solid (XI), $[RhCl(CO)\{(ClPN\text{-}Bu^t)_2\}]_n$. Chemical analysis supports this formation but low solubility in suitable solvents prohibited a molecular weight determination.

The room temperature ^{31}P.N.M.R. spectrum of the complex exhibits two resonances (-11.506, 6.257 δppm), slightly broadened (width at half height is ~60Hz), of equal intensity, indicating phosphorus donation. The ^{1}H.N.M.R. spectrum consists of a singlet (1.65 δppm) shifted slightly upfield from that of the free ligand. Infra-red data confirms the presence of carbonyl groups (2020(s) 2005(w) cm^{-1}). Two structures are possible for this complex, a monomeric species (L), analogous to $[\{Ph_2P(CH_2)_2PPh_2\}.RhCl(CO)]$[216,217] or a dimeric structure (M) such as found for $[\{Ph_2ECH_2EPh_2\}.RhCl(CO)]_2$ (E=As and P).[218,219]



L



M

In the case of the monomeric structure (L), two inequivalent phosphorus atoms are present and a doublet of doublets is expected, due to P-Rh and P-P′ couplings. In practice $J_{P-P'}$ is relatively small, in the diphosphine complex $[Ph_2P(CH_2)_2PPh_2\text{-}RhCl(CO)]$ $J_{P-P'}$ is 34Hz, and J_{Rh-P} 124 and 158 Hz for phosphorus trans to Cl and CO respectively.[217] The spectrum of the complex is well resolved at 223K but broader at room temperature. For the dimeric complex (M), one doublet is predicted for the equivalent phosphorus atoms split by coupling with rhodium. In the series of dimeric diphosphine complexes $[Ph_2P(CH_2)_nPPh_2\ RhCl(CO)]_2$ (n=1,3, and 4) splittings of the order of 120 to 130 Hz were observed.[217] It is possible to interpret our ^{31}P.N.M.R. data in two ways:-

a) that structure (L) is adopted but at room temperature the spectrum is not resolved. The peaks are slightly broad, and the large separation between the peaks (17·763 δppm, 647.Hz) seems to be more in line with that expected for the inequivalent phosphorus atoms than with J_{Rh-P} splitting. In $[Ph_2P(CH_2)_2PPh_2$-$RhCl(CO)]$ the two doublets of doublets are separated by 21.2 ppm.

b) that structure (M) is adopted. The spectrum observed is due to the equivalent phosphorus atoms split by rhodium coupling (-2.624 ppm; J_{Rh-P}=647Hz) In the latter explanation J_{Rh-P} is unusually large, and in consequence structure (L) is favoured. This is supported by the position of the carbonyl stretching band which is at high frequency (2020 cm^{-1}) comparable to that found for $[(Ph_2P(CH_2)_2PPh_2)\ RhCl(CO)]$ (2010cm^{-1}) Whereas the dimeric complexes absorb 40-60 cm^{-1} lower, eg:- $[Ph_2P(CH_2)_4PPh_2\ RhCl(CO)]_2$ at 1951 cm^{-1}. Two bands are expected for the unsymmetrical cis-chloro isomer of (M) and only one for the trans-isomer (M).[220] The infra-red data is, trans to Cl and CO respectively.[217] The spectrum of the complex is well resolved at 223K but broader at room temperature. For the dimeric complex (M), one doublet is predicted for the equivalent phosphorus atoms split by coupling with rhodium. In the series of dimeric diphosphine complexes $[Ph_2P(CH_2)_nPPh_2\ RhCl(CO)]_2$ (n=1,3, and 4) splittings of the order of 120 to 130 Hz were observed.[217] It is possible to interpret our ^{31}P.N.M.R. data in two ways:-

a) that structure (L) is adopted but at room temperature the spectrum is not resolved. The peaks are slightly broad, and the large separation between the peaks (17·763 δppm, 647.Hz) seems to be more in line with that expected for the inequivalent phosphorus atoms than with J_{Rh-P} splitting. In $[Ph_2P(CH_2)_2PPh_2$-$RhCl(CO)]$ the two doublets of doublets are separated by 21.2 ppm.

b) that structure (M) is adopted. The spectrum observed is due to the equivalent phosphorus atoms split by rhodium coupling (-2.624 ppm; J_{Rh-P}=647Hz) In the latter explanation J_{Rh-P} is unusually large, and in consequence structure (L) is favoured. This is supported by the position of the carbonyl stretching band which is at high frequency (2020 cm^{-1}) comparable to that found for $[(Ph_2P(CH_2)_2PPh_2)\ RhCl(CO)]$ (2010cm^{-1}) Whereas the dimeric complexes absorb 40-60 cm^{-1} lower, eg:- $[Ph_2P(CH_2)_4PPh_2\ RhCl(CO)]_2$ at 1951 cm^{-1}. Two bands are expected for the unsymmetrical cis-chloro isomer of (M) and only one for the trans-isomer (M).[220] The infra-red data is, therefore, consistent with structure (L). Values for ν(Rh-Cl) in the range 350-250cm^{-1} is typical for both square-planar and octahedral complexes, the precise value depending, mainly, on the ligand trans to Cl.[220,221] The broad intense band at 272 cm^{-1} and its associated shoulder at 255 cm^{-1}, in the spectrum of our complex, is assigned to ν(Rh-Cl) modes.

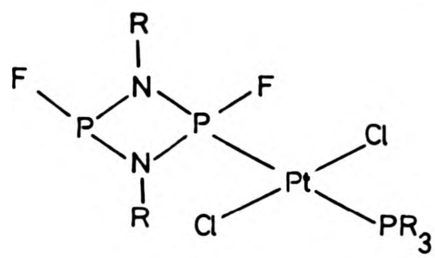
The picture that has emerged from our study of the coordination behaviour of 1,3 di(tert-butyl) 2,4 dichloro-1,3,2,4 diazadiphosphetidine, is that phosphorus donation is greatly preferred to nitrogen donation. This is seen as a result of several factors including :-

a) The bulky Bu^t groups, sterically hinder nitrogen donation.

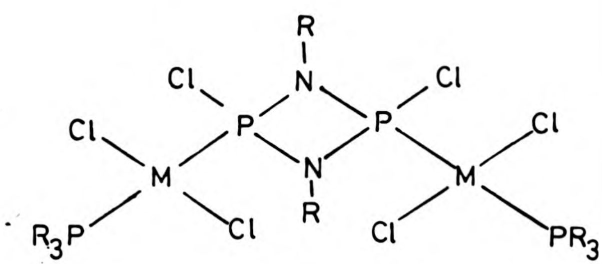
b) The delocalization of the nitrogen lone pair into the available phosphorus 3d orbitals [142,143] decreases the donor ability of the nitrogen atoms.

ADDENDUM.

In a very recent note[501], Burckett St.Laurent et al have reported the preparation of a series of platinum and rhodium complexes incorporating 1,3,2,4 diazadiphosphetidines as both mono-(**A**) and bidentate (**B**)phosphorus donors.



A



B

The complex $[ClRh\{(FPNBu^t)_2\}]_n$ reacted quantitatively with carbon monoxide giving $[RhCl(CO)\{(FPNBu^t)_2\}]$, the physical for which is apparently to be published later.

Group (VI) metal carbonyl complexes were also investigated, the major product isolated from complex product mixtures being $[M(CO)_5\{(FPNBu^t)_2\}]$ (M=Cr, Mo and W).

CHAPTER THREE.

DIIRON ENNEACARBONYL: REACTIONS WITH TETRADENTATE AMINE LIGANDS.

INTRODUCTION

As late as mid-1973 there were no known amine substituted iron carbonyl complexes, with the exception of $[Fe(CO)_4(NH_3)]$. Moreover this unique example was prepared from the reaction of the hydroxylamine-o-sulphonate ion with the $[HFe(CO)_4]^-$ anion:-[202,222,223]

$$[HFe(CO)_4]^- + H_2NOSO_3^- \longrightarrow [Fe(CO)_4(NH_3)] + SO_4^{2-}$$

which could not be generalized to amines as a whole. Only disproportionation type products were formed when various iron carbonyls were reacted with selection of amines:-[224-230]

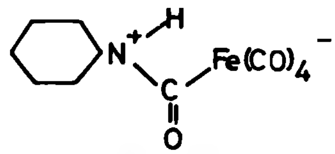
$$5Fe(CO)_5 + 6py \longrightarrow [Fe(py)_6]^{2+}[Fe_4(CO)_{13}]^{2-} + 12CO$$

$$Fe_3(CO)_{12} + 3o\text{-phen} \longrightarrow [Fe(o\text{-phen})_3]^{2+}[Fe_2(CO)_8]^{2-} + 4CO$$

$$2Fe(CO)_5 + 6NH_3 + H_2O \longrightarrow [Fe(NH_3)_6]^{2+}.2[HFe(CO)_4]^- + CO + CO_2$$

$$4Fe(CO)_5 + 3C_6H_4(NH_2)_2 \longrightarrow [Fe\{C_6H_4(NH_2)_2\}_3]^{2+}[Fe_3(CO)_{11}]^{2-} + 9CO$$

The formation of non-ionic addition compounds of the type $[Fe(CO)_5.amine]$ were suggested as precursors to the carbonylferrates.[231,232] These addition compounds were usually unstable, decomposing rapidly to give carbonylferrates. A detailed spectroscopic investigation[233] of the reactions of $Fe(CO)_5$ with piperidine at room temperature identified three different products. The first was a species formulated as $[Fe(CO)_5(C_5H_{10}NH)_3]$ which was suggested to contain the grouping (**A**). The anion $[FeH(CO)_4]^-$ and a third species



A

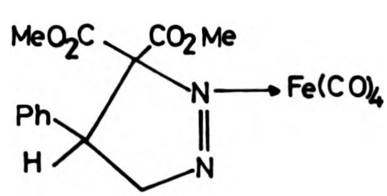
suggested to be $[Fe(CO)_4(C_5H_{10}NH)]$ were also identified, the former was thought to result from hydrolysis of $[Fe(CO)_5(C_5H_{10}NH)_3]$ by trace amounts of water in the amine.

The products obtained from these disproportionation reactions seemingly depend on the conditions e.g. reaction of $Fe_3(CO)_{12}$ with ethylenediamine:-[234]

$$Fe_3(CO)_{12} \xrightarrow[313K]{en} [Fe(en)_3][Fe_3(CO)_{11}] \xrightarrow{363K}$$

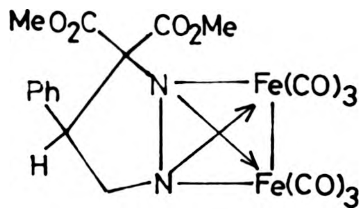
$$[Fe(en)_3][Fe_2(CO)_8] \xrightarrow{418K} [Fe(en)_3][Fe(CO)_4]$$

Reaction of iron carbonyls with various cyclic azoalkanes has resulted in the isolation of several different substitution species. Reaction of 1-pyrazolines with $Fe_2(CO)_9$ [235] yields initially (B):-

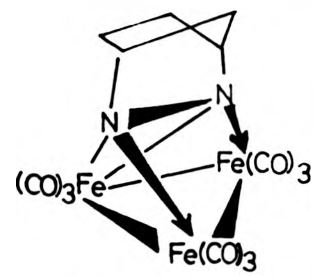


B

in which the coodinated nitrogen atom occupies an apical position in the trigonal-bipyramidal geometry around the iron atom. The geometry of the ligand is not altered by complexation,[236] and with excess $Fe_2(CO)_9$ the binuclear complex (C) is formed. This is analogous to [μ-2,3-{2,3 diazabicyclo[2,2,1] heptane}diyl-bis(tricarbonyl iron)][237,238] the structure of

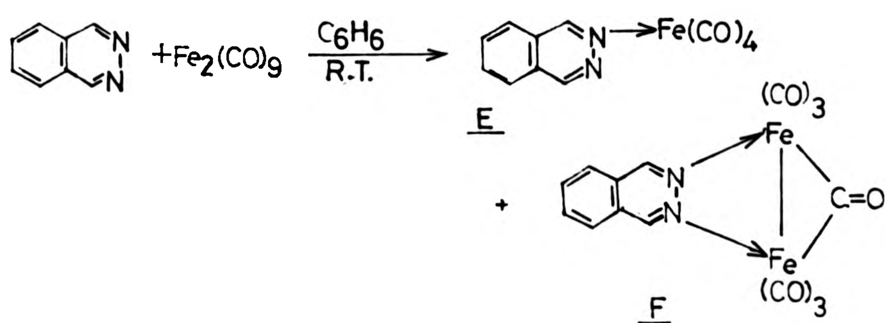


C



D

which has been confirmed by a crystal and molecular structure determination.[239] Here the two $Fe(CO)_3$ groups are linked by the two ligand nitrogen atoms through Fe-N-Fe bridges and also by an Fe-Fe bond. A N-N bond is retained in the complex, and its length is close to that expected for a single bond. With this ligand a third trinuclear complex (D) was also isolated.[240]

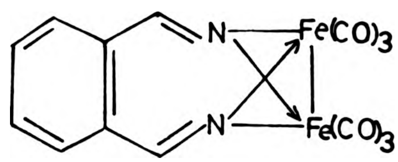


E

F

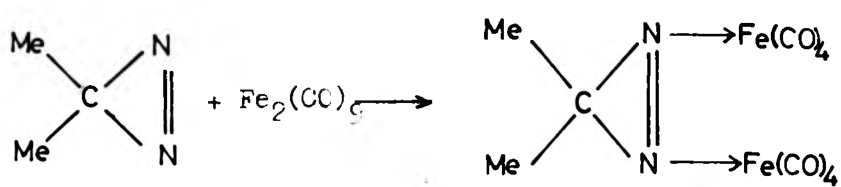
Treatment of $Fe_2(CO)_9$ with phthalazine gave $(Fe(CO)_4(phth)$ (E) as the major product and a binuclear complex (F).[241]

Compound (F) exhibits bridging as well as terminal ν(C-O) modes. On heating (E) in benzene, or alternatively by reaction of phthalazine with $Fe_2(CO)_9$ a third complex (G) was isolated, analogous to that of the 1-pyrazoline complex already mentioned.



G

A fifth type of complex is exemplified by the relatively unstable product (H) isolated at 203K from the reaction of 3,3 dimethyldiazirine and $Fe_2(CO)_9$[242].



H

Cotton and Troup[200,201,205,207] found that $Fe_2(CO)_9$ 'dissolved' in T.H.F. at R.T., the resulting 'solution' was very reactive and could be used to prepare novel substition products previously unknown. It does not appear that this is a true solution in as much that little, if any, unchanged $Fe_2(CO)_9$ is thought to be present. The course of the reaction seems to take different pathways depending on whether a carbon monoxide atmosphere is preserved above the solution or not (see also Chapter 2 section 2Bvi) It has been suggested[201] that the immediate reaction, under a positive CO pressure:-

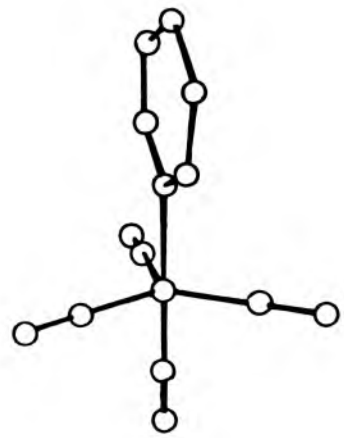
$Fe_2(CO)_9$ + T.H.F. $\longrightarrow$ $Fe(CO)_4(THF)$ + $Fe(CO)_5$

$Fe(CO)_4(THF)$, being very reactive, reacts with any donors present to give mono-nuclear products such as $[Fe(CO)_4py]$, approaching but not exceeding yields of 50% based on total iron. Triiron dodecacarbonyl is formed when no ligands are present, probably due to further reaction:-

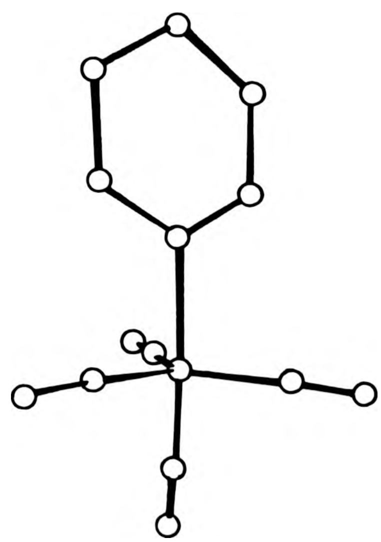
$$3[Fe(CO)_4(THF)] \longrightarrow Fe_3(CO)_{12} + 3THF$$

When an inert atmosphere is maintained in the reaction vessel polynuclear species are obtained eg; $[Fe_2(CO)_7Ph_2PCH_2PPh_2]$.[206,207]

Although the exact nature of the species present in this tetrahydrofuran 'solution', has not been elucidated, it has been utilized as a method of preparing new iron carbonyl complexes. In particular it facilitated preparation of the complexes $[Fe(CO)_4L]$ (L=py or pyr),as the first neutral complexes of the type $[Fe(CO)_{5-x}Am_x]$ (Am=Amine other than NH_3). The complexes were isolated on direct treatment of the $Fe_2(CO)_9$ /T.H.F. 'solution' with pyridine or pyrazine under a CO atmosphere.[201] The structures of the complexes are very similar, closely resembling the structure of $Fe(CO)_5$ with the substitution of one of the axial carbonyl ligands by pyridine (Fig 3.1) or pyrazine molecule. The coordination of the iron atom is trigonal bipyramidal with the axial carbonyl trans to the pyridine or pyrazine having a shorter bond distance than the average equatorial carbonyl bond distance.



a) Structure of $[Fe(CO)_4\,py]$ showing the relationship of the plane of the pyridine to the equatorial CO groups.

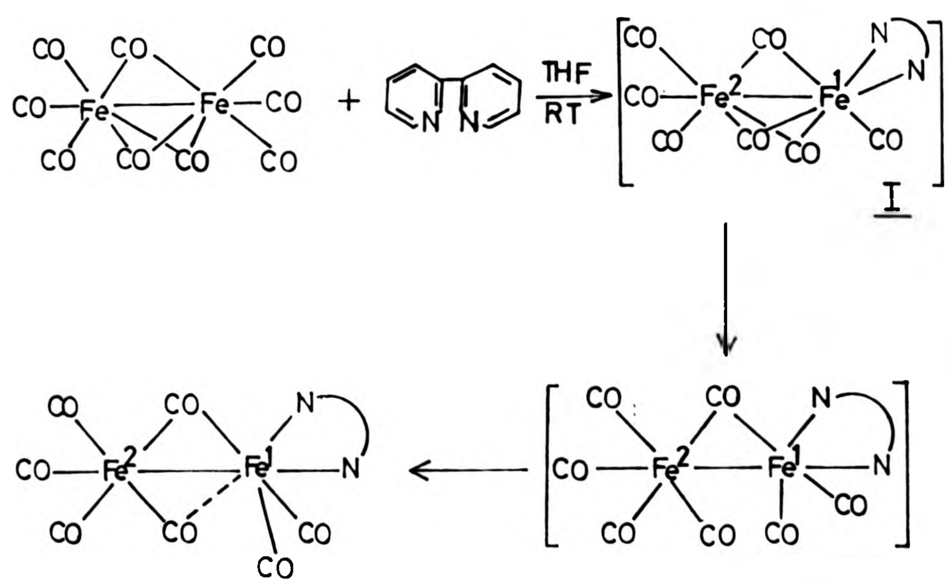


b) Structure of $[Fe(CO)_4\,pyr]$.

Fig. 3.1 Structures of the mononuclear amine complexes $[Fe(CO)_4\,Am]$ (Am = pyridine and pyrazine).

The structure persists in solution, as shown by three strong carbonyl stretching bands as predicted for a $Fe(CO)_4$ group with local C_{3v} symmetry.[63]

Bidentate amine ligands have also been reacted with $Fe_2(CO)_9$ in T.H.F. to give some interesting products. In the absence of a CO atmosphere, $Fe_2(CO)_9$ reacts with 2,2' bipyridyl in T.H.F. to afford a binuclear compound, $[Fe_2(CO)_7(bipy)]$.[205] The complex is of structural interest in that the bipyridyl ligand replaces two carbonyl groups from the same metal, leading to the formation of an S.B.C.O. group (see Fig 2.7). While this compound may be regarded as substitution product of $Fe_2(CO)_9$, rather than the result of disproportionation or other scission processes, extensive rearrangement of the structure occurrs:-



I

J

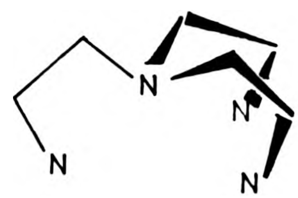
K

Bipyridyl is a good σ-donor but a poor (compared to a CO) π-acid and this means there is a need to generate π-acid capacity when it replaces the two terminal carbonyl groups as in (I). Thus two carbonyl bridges open, creating two more terminal CO's, giving structure (J). The final step is to distort one of the terminal carbonyls, bending towards the bipyridyl substituted iron (Fe(1)) atom (K). Fe(1) has a considerable negative charge and only two terminal carbonyl ligands to help in delocalizing the charge. Hence it forms a weak $d \rightarrow \pi^*$ dative bond to the carbonyl group, as mechanism to transfer electron density to a CO group on the less negatively charged Fe(2) atom. Conversely, the structure may also be regarded as a simple substitution product of an initially singly bridge structure - $(CO)_4Fe(\mu\text{-}CO)Fe(CO)_4$- which is probably only a few kilocalories less stable than the $(CO)_3Fe(\mu\text{-}CO)_3Fe(CO)_3$ structure.

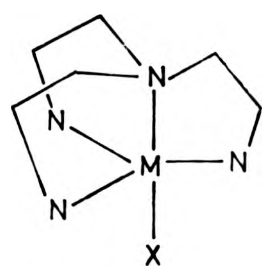
The ligand 1,2 diazine also forms a complex with the same stiochiometry, but the structure is not the same.[209] In this complex the ligand bridges the two iron atoms and is similar to the analogous complex[207], $[Fe_2(CO)_7\ (Ph_2P)_2\text{-}CH_2]$. The difference is thought to be caused by the geometries of the two diamines: bipyridyl is incapable of bridging two metal atoms that are bonded to each other, whereas 1,2 diazine is incapable of forming two bonds to the same metal atom.

We have studied the behaviour of the three potentially tetradentate amine ligands, tris (2amino ethyl) amine, (TREN), tris (2dimethylamino ethyl) amine, (Me_6TREN), and 1,4,7,10 tetraazadecane, (TRIEN), towards $Fe_2(CO)_9$ in T.H.F.

TREN and Me_6TREN take up a 'tripod' framework (L) and have been utilised to stabilize five-coordinate trigonal bipyramidal structures in many transition metal complexes, (M).[19,23,243-245]



L

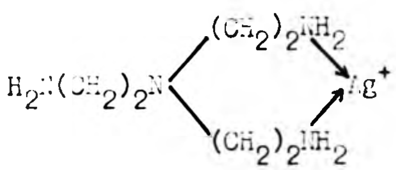


M

Additionally, both TREN[246-251] and Me_6TREN[252] have shown the ability to give six-coordinate complexes.

1,4,7,10 tetrazadecane, the linear isomer of TREN, being more flexible is capable of stabilizing various structures. The copper(II) complex ion $[Cu(TRIEN)(SCN)]^+$ adopts a square pyramidal structure [253] whereas the cobalt (III) complex

[Co(TRIEN)Cl_2]Cl is octahedral.[254] Square planar structures have also been observed.[255,256] In the vast majority of complexes of these powerful chelating ligands coordination of all four nitrogen atoms is involved. The two atoms in each of the carbon chains enable a network of three five-membered chelate rings to be formed on complexation. However, examples are known in which these ligands exhibit diminished denticity. Partial unwrapping of Cr(III)TRIEN complexes has been studied[257] and in the silver complex $[Ag(TREN)]^+$ [258] it is thought that only two of the primary amines are involved in coordination:-



In the titanium (III) and chromium (III) complexes $[MCl_3(L_4)_x]$ where L_4=TREN x= 1or 2 and L_4=Me_6TREN x =1, M=Ti and Cr) the ligands are coordinated through three nitrogen atoms.[259,260] Similarly, in [CdX_2(Me_6TREN)] (X=Cl and Br) Me_6TREN exhibits reduced denticity.[261] Since all the nitrogen donor sites of Me_6TREN have essentially the same steric requirements, metal coordination solely through the terminal -NMe_2 groups would have no obvious advantages. Spectral data for these complexes indicates that they contain a fused five-membered chelate ring system with a terminal centre as a 'dangling arm'. In contrast the analogous TREN complexes contain three eight-membered rings with the tertiary amine uncoordinated. The formation of eight rather than five-membered rings, which are normally accepted as the more stable,[262] in these complexes, is probably offset by the facts that:-

a) The tertiary amine centre is a weaker donor than the primary amine sites.[263-265]

b) Steric factors reduce the effectiveness of linked five-membered rings so that larger rings are more stable.[266]

EXPERIMENTAL

Reactions of Diiron Enneacarbonyl:-

3i With tris (2aminoethyl) amine.

$Fe_2(CO)_9$ (1.17g;3.21mmols) was placed in a ~250cm^3 capacity ampoule with 100 cm^{3}T.H.F., then TREN(0.48g; 3.30mmols), dissolved in 25cm^3 T.H.F., was slowly dripped in. The ampoule was transferred to the vacuum-line, degassed at 96K then sealed under vacuum. On warming to R.T., bubbles of gas were seen escaping from the claret solution. The pale brown solid which precipitated was collected by filtration, washed with T.H.F. until the washings were colourless; then pumped dry giving a sandy brown solid (I) (0.47g;31.8%). The filtrate was concentrated then treated with n-hexane which resulted in the precipitation of a burgandy solid (II) (0.21; 15.4%).

Sandy Brown Solid (I)

Infra-red Data. (cm^{-1}; nujol and H.C.B. mulls) 3345(w) 3275(m) 3160(w) 2975(m) 2940(m) 2880(m) 1923(s) 1862(vs,br) 1670(m,sh) 1570(s,br) 1475(m) 1440(w,sh) 1320(m) 1160(w) 1070(m) 980(m) 890(w) 820(w) 730(w) 700(m) 620(s) 510(vw)

Chemical Analysis (%) Found C:36.23, H:7.82, N:24.18, Calc'd for $C_7H_{18}N_4OFe$ C:36.54, H:7.89, N:24.35.

Burgundy Solid (II)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls and T.H.F. solution.) 3450(w,sh) 3260(m) 3150(m) 3090(w,sh) 2975(s) 2950(s) 2830(w) 2055(w) 2000(m) 1955(s,sh) 1940(vs) 1730(w) 1670(m,sh) 1570(vs,br) 1500(vs) 1450(s,sh) 1400(m) 1310(s) 1270(s) 1160(m,sh) 1100(s) 1025(s) 805(s)

730(w) 610(w) 510(vw) 475(vw) 380(vw).

Chemical Analysis. (%) Found C: 33.72, H:4.67, N:13.08,
Calc'd for $C_{12}H_{18}N_4O_6Fe$, C:33.83, H:4.26, N:13.15.

3ii With tris (2dimethylamino ethyl) amine.

$Fe_2(CO)_9$ (075g; 2.06 mmols) and T.H.F. (~100cm^3) were placed in a ~ 250 cm^3 capacity ampoule, a T.H.F. solution (~10cm^3) of Me_6TREN(0.55g; 2.39mmols) was then dripped in. The reaction mixture was degassed at 96K and then the ampoule sealed under vacuum. Slow gas evolution from the red solution occurred on warming to R.T.. After a week the solution was filtered, the solid which had precipated in this time was collected and thoroughly washed with T.H.F. and n-hexane. A pale brown solid (III) (0.49g;30.5%) was obtained on pumping dry on the vacuum line. The filtrate was concentrated to 5cm^3 then n-hexane added dropwise to preciptate a dark plum coloured solid (IV) (0.30g;28.5%).

Pale Brown Solid (III).

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2960(m) 2920(m) 2820(w) 2800(w) 2780(w) 1930(m) 1850(vs) 1470(m) 1460(m) 1300(w) 1265(m) 1100(w,br) 1030(m) 810(m) 780(m) 730(vw) 620(m)

Chemical Analysis (%) Found, C:49.86, H:9.89, N:17.86,
Calc'd for $C_{13}H_{30}N_4OFe$, C:49.69, H:9.62, N:17.83.

Plum Solid (IV).

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls, T.H.F. solution) 2940(s) 2890(s,br) 2840(s) 2780(m,sh) 2700(w) 2060(w)

1990(vs) 1940(vs) 1835(s) 1725(m) 1460(w) 1445(m) 1430(w) 1290(m) 1260(w) 1170(w) 1150(w) 1100(m) 1040(m) 1020(m) 1005(w) 935(w) 905(vw) 800(m) 770(m) 730(v,sh) 720(w) 675(s) 640(m) 610(m) 580(m).

Chemical Analysis (%) Found C:42.26, H:5.68, N:10.91, Calc'd for $C_{18}H_{30}N_4O_6Fe_2$, C:42.38, H:5.93, N:10.98.

3iii With 1,4,7,10 Tetraazadecane.

TRIEN (0.42g;2.89 mmols) dissolved in ~10cm^3 T.H.F. was slowly dripped onto $Fe_2(CO)_9$(0.95g; 2.62 mmols) in T.H.F. (~100cm^3). The resulting mixture was degassed and sealed at 96K. Bubbles of gas were evolved from the red-brown solution produced on warming to R.T. After a few days a pale brown precipitate deposited. A buff solid (V) (o.46g;38%) was obtained by filtration of the mixture, followed by thorough washing with T.H.F. and n-hexane and drying in vacuo. The filtrate yielded a dark maroon solid (VI) (0.24g;21.5%) after concentration and addition of n-hexane.

Buff solid (V)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 3340(w,sh) 3240(m,br) 3210(w,sh) 3140(w) 2940(m) 2910(m) 2860(m) 2810(v,sh) 1910(vs) 1855(vs,br) 1650(w,sh) 1565(s,br) 1465(m,br) 1300(m) 1160(w) 1060(w) 1035(w) 990(w) 810(w) 720(vw) 695(w) 610(m) 500(vw)

Chemical Analysis (%) Found, C:36.92, H:7.78, N:25.54, Calc'd for $C_7H_8N_4OFe$, C:36.54, H:7.89, N:24.35.

Maroon Solid (VI)

Infra-red Data (cm^{-1}; nujol and H.C.B. Mulls and T.H.F. solution)

3400(m,sh) 3320(s) 3260(s,br) 3150(m,sh) 3090(m,sh)
3030(m) 2940(s,sh) 2920(s) 2870(s) 2820(s) 2060(w)
2040(w) 1995(vs) 1940(vs) 1910(vs) 1850(vs) 1760(m)
1730(w) 1650(m,br) 1565(s,br) 1480(m,br) 1430(m,br)
1285(s) 1270(s,sh) 1170(w) 1150(m) 1060(m,br) 1030(m,br)
980(w) 930(w) 800(m) 720(w) 675(s) 610(s) 585(s).

Chemical Analysis (%) Found, C:33.68, H:4.12, N:12.92,
Calc'd for $C_{12}H_{18}N_4O_6Fe_2$, C:33.83, H:4.26, N:13.15.

DISCUSSION

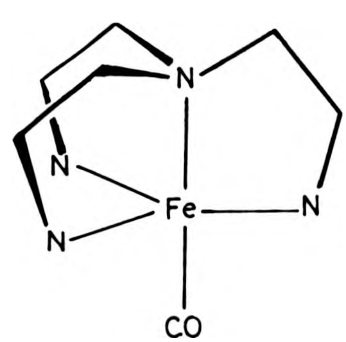
The first point that emerges from this study is that $Fe_2(CO)_9$ reacts with TREN, Me_6TREN and TRIEN, to give two series of products which analysed for $Fe(CO)L_4$ and $Fe_2(CO)_6L_4$ (L_4=TREN, Me_6TREN and TRIEN) respectively.

3i With tris (2-amino ethyl) amine.

The reaction was carried out in a closed reaction vessel so that a slight partial pressure of carbon monoxide builds up above the solution. The mononuclear complex Fe(CO)(TREN) precipitates from the T.H.F. solution as a sandy brown solid (I). The binuclear complex was soluble in T.H.F. but precipitates on addition of n-hexane as a burgundy solid (II).

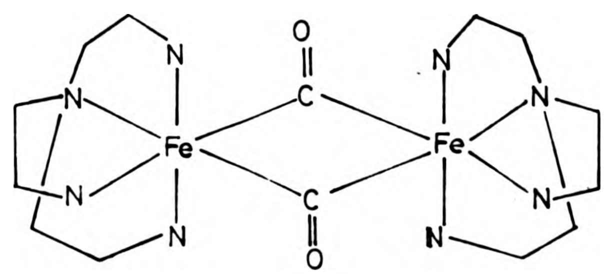
3ia The Mononuclear Complex (I).

For the mononuclear complex Fe(CO)(TREN) the 'obvious' structure would seem to be a trigonal bipyramidal arrangement (A)



(A)

Here the amine ligand is coordinated through all four nitrogen atoms and the carbonyl group occupys an axial position, analogous to many other TREN complexes including $[M(TREN)X]^+$ (M=Cu,X=NCS,Cl)[19]. However, this type of structure is predicted to give rise to only one carbonyl stretching mode.[63] Our complex exhibits two infra-red bands in this region (Table 3.1) Analytical data procludes the possibility of more than one carbonyl group per TREN molecule which eliminates formulations of the type $Fe(CO)_2(TREN)$. The high frequency observed for these two bands essentially rules out the possibility of a dicarbonyl bridged binuclear species, e.g. (B).



B

Furthermore, the i.r. data suggests that the ligand is not tetradentate. In complexes of this type, the CH_2 rocking modes of the metal-chelate ring generally lie between 900-750cm^{-1}. It has also been found[245,248,254,267,268] that when a metal complex contains two or more five-membered chelate rings that are non-coplanar, two CH_2 rocking modes are observed. If all the rings are coplanar, there is only one. Only one band,

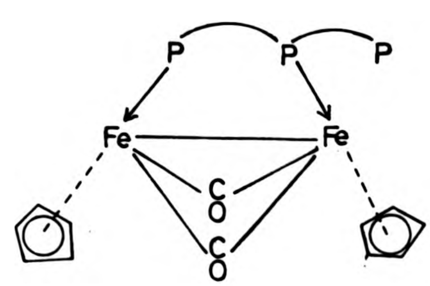
Table 3.1 Selected infra-red data for the tetradentate ligands, TREN, Me_6TREN and TRIEN and their iron carbonyl complexes (cm^{-1}).

TREN	Fe(CO)L (I)	$Fe_2(CO)_6L$ (II)	Me_6TREN	Fe(CO)L (III)	$Fe_2(CO)_6L$ (IV)	TRIEN	Fe(CO)L (V)	$Fe_2(CO)_6L$ (VI)
3360(s)	3345(w)					3350(m)	3340(w,sh)	3320(s)
3280(s)	3275(m)	3260(m)				3265(s)	3240(m)	3260(s,br)
3205(m,sh)	3160(m)	3150(m)					3140(w)	3150(m,sh)
	2975(m)	2975(s)	2950(s,sh)	2960(m)	2940(s)		2940(m)	3030(m)
2925(s)	2940(m)	2950(s)	2930(s)	2920(m)	2890(s,br)	2930(vs)	2910(m)	2920(s)
	2880(m)	2830(w)	2825(m)	2820(w)	2840(s)		2860(m)	2870(s)
2800(s)			2805(s)	2800(w)		2800(vs)		2820(s)
			2755(S)	2780(w)	2780(m,sh)			
					2700(w)			
		2055(w)			2060(w)			2060(w)
		2000(m)						2040(w)
					1990(vs)			1995(vs)

Table 3.1 continued.

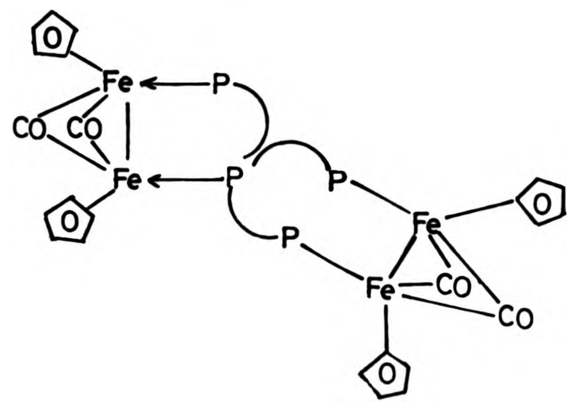
		1940(vs)			1940(vs)			1940(vs)
	1923(s)			1930(m)	1910(s)		1910(vs)	1910(vs)
	1862(vs,br)			1850(vs)	1835(s)		1855(vs)	1850(vs)
								1760(m)
		1730(w)		1480(m,sh)	1725(m)			1730(w)
	1475(m)			1475(s)				
1450(s)	1440(w,sh)	1450(s,sh)	1455(s)	1460(m, sh)	1460(w)	1450(s)	1465(m)	1480(m)
		1400(m)	1400(w)		1445(w)			1430(m,br)
900(s)					905(w)	905(s)		
860(s)	890(w)					840(s)		
	820(w)	805(s)		810(m)	800(m)		810(w)	800(m)
				780(m)	770(m)			

at 820 cm^{-1}, assignable to a CH_2 rocking mode, can be located in the infra-red spectrum of our product. In the 3500-3100cm^{-1} region, TREN exhibits two bands (3358 and 3282cm^{-1}) assigned to the ν_{as}(NH) and ν_s(NH) modes of the primary amine groups. In our complex, these bands are shifted to lower frequency and have become more complex (3345(w) 3275(m) and 3160(w) cm^{-1}) The reduction in frequency is characteristic of amine coordination.[269] Moreover, since more than two bands are observed it would seem that the primary amines are not in identical environments.[270] The spectral evidence points to reduced denticity of the amine ligand. As noted in the introduction complexes in which TREN is denied a tetradentate role are not common. Interestingly, a selection of polydentate tertiary phosphines have been shown to exhibit reduced denticity on reaction with cyclopentadienyl iron carbonyl compounds.[271-274] For example, the potentially tridentate ligand $\{Ph_2P(CH_2)_2\}_2PPh_2$ only coordinates through two phosphorus atoms[271] (C).



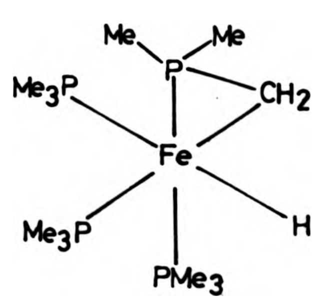
C

With the tripod ligand $\{Ph_2P(CH_2)_2\}_3P$, however, a tetra-metallic complex (D) was obtained.[272]



D

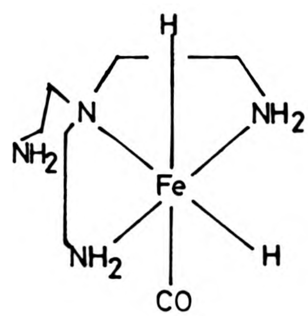
Hydride formation is not uncommon in the reactions of metal carbonyls, the hydrogen being abstracted from the solvent or the ligand. For instance, the anion $[FeH(CO)_4]^-$ is formed on reaction of iron pentacarbonyl with piperidine. This is thought to be due to hydrolysis, residual water being present inspite of drying over KOH[233]. The trimethylphosphine complex $[Fe(PMe_3)_5]$ is actually a hydride containing complex (E), through abstraction of hydrogen from the ligand [275].



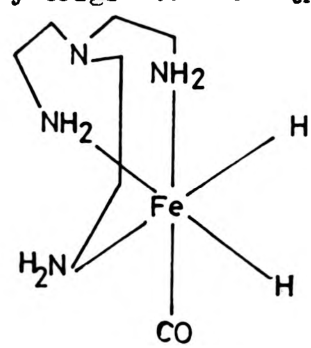
E

Accepting that the infra-red data for our mononuclear

TREN complex(I) precluded structure (A), one possible formulation is that we have a hydride species, e.g. $Fe(CO)(TREN)H_2$. This could not be differentiated from Fe(CO)(TREN) by chemical analysis. Both structures (F) and (G) are consistent with the infra-red data discussed previously, the hydrogen atoms may originate from the solvent.



F

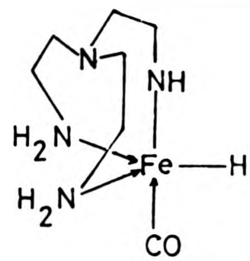


G

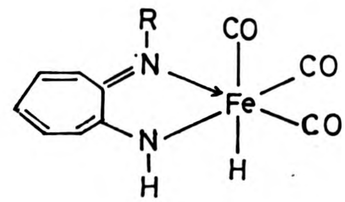
Since the primary amine groups will bind more strongly than the tertiary amine group,[263-265] structure (G) is preferred.

Metal-hydrogen stretching modes occur in the region $2200\text{-}1700cm^{-1}$,[376] ie. in the region also associated with carbonyl stretching vibrations. The two absorptions observed, for the complex, in this region are thus assigned to a ν(C-O) and a ν(Fe-H). Table 3.2 gives selected infra-red data for some comparable systems.

Insertion of the iron atom into an N-H bond is also possible, eg (H), similar to the insertion into a C-H bond as noted in (E) and in $[HFe(Ph_2P(CH_2)_2PPh_2)\{Ph(C_6H_4)P(CH_2)_2PPh_2\}]$.



H



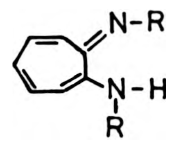
I

Table 3.2 Selected infra-red data for some carbonyl hydride complexes.

Complex	(C-O) (cm^{-1})	(M-H) (cm^{-1})	Ref.
$H_2Fe(CO)(PEtPh_2)_3$	1900	1875	277
$H_2Fe(Ph_2P(CH_2)_2PPh_2)_2.C_6H_6$		1840	278
$H_2Fe(PMe_3)_4$		1795	
$Fe(C_{22}H_{22}N_4)(CO)$	1920		280
$Fe(CO)(Me_2AsC_6H_4AsMe_2)_2$	1953		281
$HFe(Cl_3Si)_2(C_5H_5)(CO)$	2025	1960	282
$HFe(PMe_3)_3\ PMe_2(CH_2)$		1820	275
$HFe(Ph_2P(CH_2)_2PPh_2)$- $Ph(C_6H_4)P(CH_2)_2PPh_2$		1893	278
$H_2Fe(TREN)(CO)$	1923	1862	

An unstable Fe-H containing species (I) was proposed

as an intermediate in the reaction of $Fe(CO)_5$ with the disubstituted aminotropeneimines (ATI) of the type:-[283]



where R=Me,Et,Bu^t,Ph,p-MeC_6H_4. The proposed mechanism involved replacement of two carbonyl groups:-

The second step in the reaction is then transfer of a hydrogen to the iron atom to give (I) as an intermediate, the final product being $Fe^{III}(ATI)_3$.

It was unfortunate that our mononuclear TREN complex was completely insoluble in all of the common organic solvents denying a ^{1}H.N.M.R. spectrum and possible location of a metal hydride resonance. A mass spectrum of the complex gave a highest $\frac{m}{e}$ value of 146 assigned to TREN$^+$, indicating decomposition of the complex in the source. The proposed formulations for the product therefore rests on infra-red spectral data and chemical analysis.

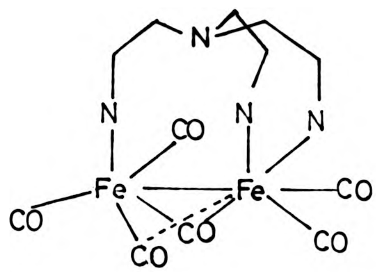
3ib The Binuclear Complex (II)

The infra-red spectrum of the binuclear complex (II), $Fe_2(CO)_6$(TREN), also indicates a non-tetradentate attachment of the ligand. Only one CH_2 rocking mode could be located, at 805cm^{-1}, and a complex profile in the ν(N-H) stretching region was observed (3450(w,sh) 3260(m,br) 3150(m,sh) 3090(w,sh) cm^{-1}). The complex exhibits bands attributable to terminal carbonyl stretching modes at 2055(w) 2000(m) 1955(s,sh) and 1940(s) cm^{-1}, with some evidence for a very weak band at 1730cm^{-1} assignable to a bridging carbonyl grouping. In the event of terdentate behaviour, the resulting binuclear complex must be unsymmetrical. However no ν(C-O) stretching mode associated with a S.B.C.O. group, usually found in these asymmetric complexes,[200] could be located. Comparison of the number and position of the carbonyl bands with literature data for carbonyl ferrate anions (Table 3.3) rules out an ionic formation, eg. $[Fe(TREN)_2]^{2+}[Fe_3(CO)_{11}]^{2-}$

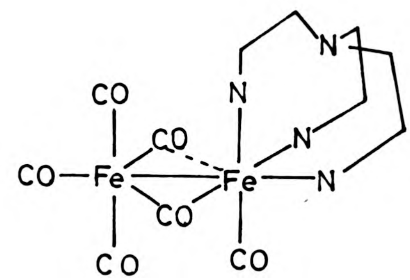
Table 3.3 Carbonyl stretching vibrations of the carbonyl ferrate anions.[233]

Anion	ν(C-O)(cm^{-1})				
$[Fe(CO)_4]^{2-}$	1730(s)				
$[HFe(CO)_4]^-$	2008(w)	1914(m)	1880(s)		
$[Fe_2(CO)_8]^{2-}$	1916(m)	1866(s)	1842(w)		
$[HFe_2(CO)_8]^-$	1998(w)	1980(m)	1930(s)	1906(m)	1873(w)
$[Fe_3(CO)_{11}]^{2-}$	1941(s)	1913(m)	1884(w)		
$[HFe_3(CO)_{11}]^-$	2070(w)	2004(s)	1980(m)	1950(w)	
$[Fe_4(CO)_{13}]^{2-}$	2030(w)	1967(s)	1950(m)	1829(vw)	

At this stage it is only possible to surmise the type of structure involved for this complex (II), possibilities include (J) and (K).



J



K

N.M.R. spectral data could not, unfortunately, be obtained due to rapid decomposition in the only suitable solvent, d^6 DMSO.

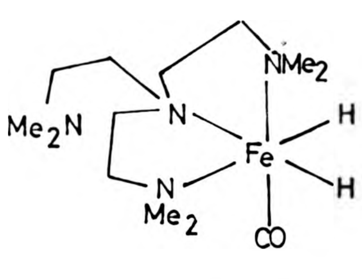
3ii With tris (2 dimethylamino ethyl) amine.

Reaction of Me_6TREN with $Fe_2(CO)_9$ in T.H.F. gives two products, viz., a T.H.F. insoluble brown solid (III) which analysed for [Fe(CO)(Me_6TREN)] , and a T.H.F. soluble plum solid (IV) which analysed for [$Fe_2(CO)_6$(Me_6TREN)] .

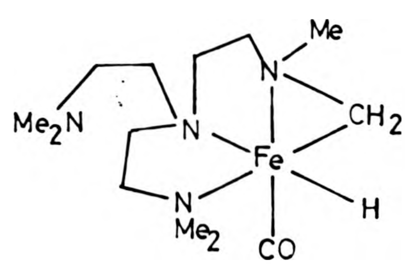
3iia The Mononuclear Complex (III)

The mononuclear complex [Fe(CO)(Me_6TREN)] exhibits infra-red absorptions in the region 2200-1700cm^{-1}, inconsistent with a simple five-coordinate formulation (A). In contrast to the analogous TREN complex, two CH_2 rocking modes can be located at 810(m) and 780(m) cm^{-1}, indicating the presence of two or more non-coplanar chelate rings. The appearance of bands (2820(w) 2800(w) and 2780(w) cm^{-1}) in the region 2850-2750cm^{-1} is characteristic of an un-coordinated $-NMe_2$ group,[284,285] implying non-tetradentate attachment. It may be noted that, in metal complexes of the multidentate ligand, 1,4,7 triazaheptane (DIEN), fac - octahedral structures, where there are two non-coplanar chelate rings, exhibit three absorptions in the CH_2 wag region ($1500\text{-}1400cm^{-1}$). Our complex (III) shows the same profile in this region, as a strong peak ($1475cm^{-1}$) with a distinct shoulder to both high ($1480cm^{-1}$) and low ($1460cm^{-1}$) energy. The accumulated infra-red data is consistent with a structure in which the ligand is coordinated through three nitrogen atoms with an uncoordinated 'dangling' arm.

As in the analogous TREN complex, a carbonyl hydride species is proposed eg (L) or (M). The carbonyl stretching band, of which, is located at $1950cm^{-1}$ and the metal-hydride stretching mode at $1850cm^{-1}$.



L



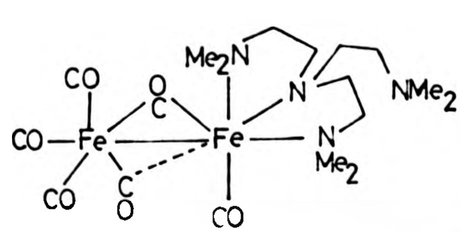
M

3iib The Binuclear Complex (IV)

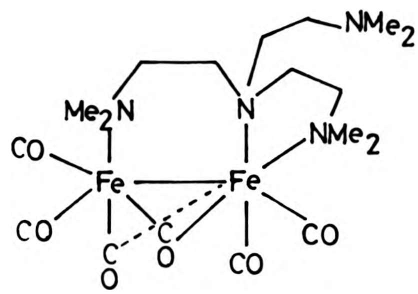
As in the mononuclear complex (III), two bands assignable to CH_2 rocking modes can be located (800(m) and 770(m) cm^{-1}) in the infra-red spectrum of the complex. Further a series of bands to the low energy side of the 'normal' CH absorptions

2840(s) 2780(m,sh) and 2700(w)cm^{-1}) and the CH_2 wag profile (1460(w,sh) 1445(m) and 1430(w)cm^{-1}) give strong evidence that the Me_6TREN is, again, not tetradentate. The carbonyl stretching pattern is different to that of the analogous TREN complex, bands at 2060(w) 1990(vs) 1940(s,br) 1910(s) 1835(s) and 1725(m)cm^{-1} being observed. The lowest energy band is indicative of a bridging carbonyl group. The band at 1835cm^{-1} may be due to a semi-bridging carbonyl group, but since amines are known to lower carbonyl stretching frequencies this can only be a tentative assignment.

Of the common organic solvents, only T.H.F. and DMSO were found to dissolve complex (III) to any appreciable extent. This made the collection of NMR data difficult. The ^{1}H.N.M.R. spectrum of a d^6-DMSO solution of the complex contained a multiplet resonance at 3.58 δppm, due to the methylene backbone. A second resonance for the methylene backbone and a resonance for the $-NMe_2$ protons was not observed. These are presumably obscured by the peak due to the residual protons in the solvent (2.50δppm). The solution was not concentrated enough to obtain ^{13}C.N.M.R spectra. Without further data, structures such as (N) and (P) are purely speculative.



N



P

3iii With 1,4,7,10 Tetraazadecane.

Two products were obtained from this reaction; a buff solid (V) which precipitated from the T.H.F. solution and a T.H.F. soluble, maroon solid (VI). The former analysed for [Fe(CO) (TRIEN)]and the latter [$Fe_2(CO)_6$ (TRIEN)].

3iiia The Mononuclear Complex (V)

As with the analogous TREN and Me_6TREN complexes the infra-red spectral evidence indicates that TRIEN is not coordinated by all four nitrogens. A broad complex profile, (3340(w,sh) 3240(m,br) 3210(w,sh) and 3140(w)cm^{-1}), little shifted from that of free TRIEN, is observed in the (N-H) stretching region of the spectrum. Only one band assignable to a CH_2 rocking mode can be located at 810 cm^{-1}. The 2200-1700cm^{-1} region contains two bands, inconsistent with a simple five-coordinate structure. Again, a carbonyl hydride structure is suggested, with ν(M-H) being located at 1855cm^{-1} and ν(C-O) at 1910 cm^{-1}.

3iiib The Binuclear Complex (VI)

The carbonyl stretching region of the binuclear complex, [$Fe_2(CO)_6$(TRIEN)], is similar to that of the analogous Me_6TREN complex, see above. Both terminal (2060(w) 2040(w)

1995(vs) 1940(vs) and 1910(vs)cm^{-1}) and bridging modes (1760(m) and 1730(w)cm^{-1}) are indicated. A band at 1850(vs)cm^{-1} is also observed, this is low for terminal modes and is possibly due to a S.B.C.O. group. One CH_2 rocking mode located at 800cm^{-1}, is indicative of coplanar chelate rings. The ν(N-H) stretching profile is complex (3400(m,sh) 3320(s) 3260(s) 3150(m,sh) 3090(m,sh) and 3030(m)cm^{-1}) suggesting non-tetradentate coordination. The low solubility of the complex in suitable solvents procluded the acquistion of ^{1}H.N.M.R. data.

CHAPTER FOUR.

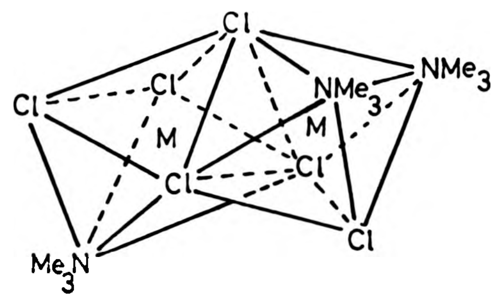
OBSERVATIONS ON THE MCl_3/NMe_3 (M= Ti,V AND Cr) SYSTEMS.

INTRODUCTION

The tervalent metal halides of the early transition metals, MX_3(M=Ti,V,Cr, X=Cl,Br,I) are polymeric via halogen-bridging. Fission of the halogen bridges does not occur unless solvents of significant polarity are used and consequently they only form monomeric adducts with strong donors. The monomeric adducts are more reactive, and undergo substitution reactions far more readily than the polymeric halides undergo the corresponding addition reactions. They are, therefore, frequently used as starting materials in the preparation of new complexes.[286-288] The most widely employed adducts are of the formulation $MX_3.3L$ (L=py,MeCN and T.H.F.) as high purity products can be readily obtained in high yields simply by soxhlet extraction of the relevant halide with the ligand for a few hours.[289-292] The monomeric five-coordinate species $MX_3(NMe_3)_2$(M=Ti,V and Cr, X=Cl and Br)[291,293-299] being coordinatively unsaturated are extremely labile and are potentially useful starting material. Previous work in this laboratory, centred on the chemistry of these species as exemplified by $CrCl_3(NMe_3)_2$ found that substitution reactions were not always straight forward. Two competing reactions may take place, one being substitution[259,300-303] the other decomposition of the five-coordinate adducts to give $[M_2Cl_6(NMe_3)_3]$ species.[304,305] Loss of NMe_3 from $MCl_3(NMe_3)_2$ is irreversible.

$$2\ MCl_3(NMe_3)_2 \ \underset{xsNMe_3}{\overset{benzene}{\rightleftharpoons}} \ [M_2Cl_6(NMe_3)_3] + NMe_3$$

The trimethylamine lacks the donor strengh to break the metal-halogen bonding in the decomposition product (A) and force the octahedral metal back to five-coordination.



A

With stronger donors, eg pyridine, the metal-halogen bonds are broken and the six-coordinate, monomeric adducts MCl_3L_3 are obtained.

The $[MCl_3(NMe_3)_2]$ complexes may be used as starting materials provided the rate of the substitution reaction (R_s) is faster than decomposition (R_d) (a).

$$MCl_3(NMe_3)_2 \xrightarrow[(a)]{+L;\ R_s > R_d} MCl_3.xL + 2NMe_3$$

$$MCl_3(NMe_3)_2 \xrightarrow[(b)]{+L;\ R_s < R_d} \tfrac{1}{2}[M_2Cl_6(NMe_3)_3] + NMe_3 + L$$

When this condition is satisfied, the complexes have been found to be useful starting materials[259,300-304] eg, in the preparation of $[MCl_3L]$ and $[ML_2]Cl_3$ (M=Ti and Cr,L=TREN).

The $[MCl_3(NMe_3)_2]$ complexes are usually prepared by direct treatment of the appropriate anhydrous metal halide with an excess of NMe_3.[294,295] Fortuitously, all are soluble in the parent amine, giving intense coloured solutions, and can be directly obtained by filtration and back-distillation within a double ampoule reaction vessel. On preparing these adducts, for possible use as starting materials where we thought easily displaced ligands would be an advantage (eg. Chapter 6), we observed that some insoluble material was always left in the reaction vessel. We were interested to determine whether this insoluble residue was simply unreacted starting material or in fact a second product of the reaction. With vanadium (III) bromide, Duckworth, Fowles and Greene[295] did isolate $[VBr_3(NMe_3)]$ as well as $[VBr_3(NMe_3)_2]$, but no similar behaviour has been described with titanium (III) or chromium (III). Closer investigation of the three systems confirmed our suspicions and we identified further products in these reactions, namely the mono-amine adducts $[MCl_2(NMe_3)]$ (M=Ti and Cr) and $[VCl_3(NMe_3)]$.

EXPERIMENTAL

Reaction of trimethylamine:-

4i With Titanium (III) Chloride

$TiCl_3$(1.5g;9.72mmols) was placed in a double ampoule, and NMe_3 (~25cm^3) distilled on under vacuo. The ampoule was sealed, and careful filtration and back distillation until a colourless solution was obtained gave the soluble $TiCl_3(NMe_3)_2$ product in one flask and a small quantity of a grey solid **(I)** (~0.1g;5%) in the other. The grey product was washed with CH_2Cl_2,MeCN and C_6H_6, then pumped dry.

Grey Solid (I).

Infra-red Data (cm^{-1};nujol mull only) 1245(m) 1145(w) 1040(w) 1015(w) 990(s) 885(m) 840(m) 805(m) 720(m) 440(w) 394(vs,br) 353(s,br) 260(m) 185(s,br).

Chemical Analysis (%) Found C:19.8, H:5.3, N:7.5, Cl:39.0

Calc'd for $C_3H_9NCl_2Ti$,C:20.25, H:5.10, N:7.87, Cl:39.85.

4ii With Vanadium (III) Chloride.

VCl_3(1.5g;9.54mmols) was sealed in a double ampoule with NMe_3 (~25cm^3). Extraction of the solid with the NMe_3, to remove the soluble $VCl_3(NMe_3)_2$ complex, until a colourless solution resulted, left a chocolate brown insoluble residue. The brown solid (II) (0.83g;41%) was washed with CH_2Cl_2, MeCN and C_6H_6 and pumped dry.

Brown solid (II).

Infra-red Data (cm^{-1};nujol and H.C.B.mulls)3130(S) 3015(m) 2950(m) 2710(w,sh) 2640(m,br) 2500(vw) 2475(w) 2340(vw) 1465(S) 1450(s,sh) 1445(s) 1410(w) 1380(s) 1255(m)

EXPERIMENTAL

Reaction of trimethylamine:-

4i With Titanium (III) Chloride

$TiCl_3$(1.5g;9.72mmols) was placed in a double ampoule, and NMe_3 (~25cm^3) distilled on under vacuo. The ampoule was sealed, and careful filtration and back distillation until a colourless solution was obtained gave the soluble $TiCl_3(NMe_3)_2$ product in one flask and a small quantity of a grey solid (I) (~0.1g;5%) in the other. The grey product was washed with CH_2Cl_2,MeCN and C_6H_6, then pumped dry.

Grey Solid (I).

Infra-red Data (cm^{-1};nujol mull only) 1245(m) 1145(w) 1040(w) 1015(w) 990(s) 885(m) 840(m) 805(m) 720(m) 440(w) 394(vs,br) 353(s,br) 260(m) 185(s,br).

Chemical Analysis (%) Found C:19.8, H:5.3, N:7.5, Cl:39.0

Calc'd for $C_3H_9NCl_2Ti$,C:20.25, H:5.10, N:7.87, Cl:39.85.

4ii With Vanadium (III) Chloride.

VCl_3(1.5g;9.54mmols) was sealed in a double ampoule with NMe_3 (~25cm^3). Extraction of the solid with the NMe_3, to remove the soluble $VCl_3(NMe_3)_2$ complex, until a colourless solution resulted, left a chocolate brown insoluble residue. The brown solid (II) (0.83g;41%) was washed with CH_2Cl_2, MeCN and C_6H_6 and pumped dry.

Brown solid (II).

Infra-red Data (cm^{-1};nujol and H.C.B.mulls)3130(S) 3015(m) 2950(m) 2710(w,sh) 2640(m,br) 2500(vw) 2475(w) 2340(vw) 1465(S) 1450(s,sh) 1445(s) 1410(w) 1380(s) 1255(m)

1230(w) 1150(vw) 1100(w) 1045(m) 1020(vw,sh) 990(s) 970(s) 940(vw) 845(m) 810(m) 720(m) 620(w) 386(m) 358(vs) 317(vs,br) 286(s) 204(s,br) 148(m).

Chemical Analysis (%) Found, C:16.5, H:4.4, N:6.7, Cl:49.0, Calc'd for $C_3H_9NCl_3V$, C:16.9 , H:4.2, N:6.5, Cl:49.1.

4iii With Chromium (III) chloride.

$CrCl_3$(1.5g;9.47mmols) was sealed in a double ampoule with NMe_3 (~25cm^3). After 2 weeks the blue-purple solution of $CrCl_3(NMe_3)_2$ developed and was filtered into the other flask. Extraction of the reaction flask with NMe_3 left a trace of pale grey solid (III) (~0.1g;5%), which was washed with CH_2Cl_2, MeCN and C_6H_6 and pumped dry.

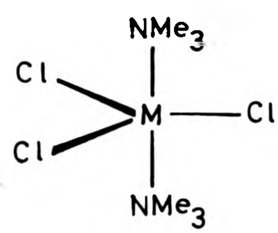
Grey Solid (III)

Infra-red Data (cm^{-1}; nujol and H.C.B.mulls) 3060(m) 3020(s) 2958(vs) 2922(vs) 2850(w) 2785(w) 2740(s) 2460(w) 1475(s) 1455(s) 1405(w) 1370(w) 1255(w) 1225(w) 1210(w) 1015(w) 975(vs) 900(w) 810(s) 755(vs) 645(w) 615(w) 545(w,sh) 500(m) 480(w,sh) 460(w,sh) 392(vs,br) 340(s,br) 228(s) 192(s,br).

Chemical Analysis (%) Found, C:19.8, H:5.4, N:7.3, Cl:38.5 Calc'd for $C_3H_9NCl_2Cr$, C:19.8, H:5.0, N:7.7, Cl:39.0.

DISCUSSION

The main products of the reaction of trimethylamine with the tervalent metal halides, MCl_3(M=Ti,V and Cr) are the bis-adducts, $[MCl_3(NMe_3)_2]$. These complexes are monomeric and of trigonal bipyramidal geometry in the solid state.[296-298] The two bulky amine groups are positioned trans, occupying the axial positions of the polyhedron (B), thus acheiving maximum separation. Distortions from pure D_{3h} symmetry are



B

found in equatorial bond angles, eg $CrCl_3(NMe_3)_2$ has two angles of 124.2° and one of 111.6°. For the titanium (III) and chromium (III) adducts, this distortion can be rationalized in terms of a Jahn-Teller distortion. In the case of vanadium (III), however, free from possible Jahn-Teller distortion, it would seem to result from a crystal packing effect. Five rather than six-coordination, in these complexes, results from steric rather than electronic factors, the bulky nature of the ligand overcoming the metal preference for an octahedral structure.

With vanadium (III), a second product of comparable percentage yield is also obtained, which we identified as the mono-adduct [$VCl_3(NMe_3)$]. In the cases of Ti(III) and Cr(III), we found no similar complexes, [$MCl_3(NMe_3)$], but small yields of the reduced complexes [$MCl_2(NMe_3)$] were obtained. It is conceivable that the analogous vanadium (II) complex may be formed but no such species could be isolated. The infra-red spectra of all three complexes confirms the presence of coordinated NMe_3, eg. the asymmetric and symmetric C-N stretching modes and the CH_3 rocking mode, observed at 1272, 826 and 1043 cm^{-1}, respectively, in the free amine[306], all shift to lower energy (Table 4.1)

Differentiation between M-Cl terminal and M-Cl bridging stretching frequencies is not clear, but the complexes are almost certainly polymeric, via halogen bridging.

Reduction of MCl_4 (M=Ti and V) by NMe_3 has been utilised as a preparative route to the corresponding tervalent, [$MCl_3(NMe_3)_2$], species.[291,307] In the case of M=Zr and Hf, where reduction is much less likely, the simple addition complexes [$MCl_4(NMe_3)_2$] are obtained.[308,309] For the VCl_4 reduction in particular, Kiesel and Schram[307] identified the main oxidation product as $Me_2NCH_2^+$. The infra-red spectrum of the product mixture, obtained on reduction of VCl_4 with a deficiency of NMe_3, clearly indicated its presence, with location of ν(C=N) at 1696cm^{-1}. In the presence of excess NMe_3 this species may undergo further reaction.

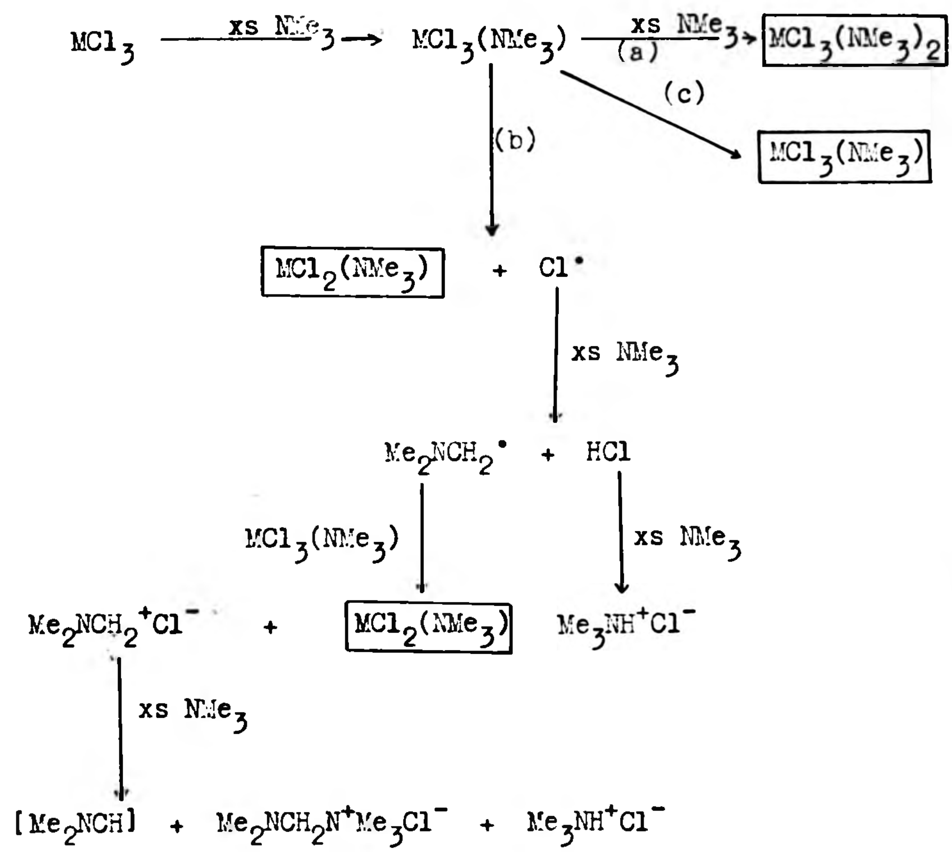
$$Me_2NCH_2^+ \;+\; VCl_4(NMe_3) \longrightarrow VCl_3(NMe_3) \;+\; Me_2NCH_2^+Cl^-$$

$$Me_2NCH_2^+Cl^- \;+\; NMe_3 \longrightarrow [Me_2NCH] \;+\; Me_3NH^+Cl^-$$

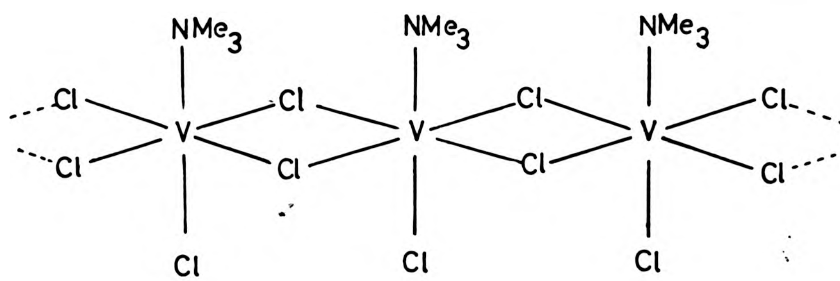
Table 4.1 Selected infra-red data for the trimethylamine complexes of MCl_3 (M=Ti, V and Cr) (cm^{-1}).

NMe_3=L	$TiCl_3L_2$	$TiCl_2L$	VCl_3L_2	VCl_3L	$V_2Cl_6L_3$	$CrCl_3L_2$	$CrCl_2L$	Assignments
1272	1238	1245	1240	1255	1251	1240	1255	$\nu_{as}CN$
	1225			1230			1225	
1043	988	990	983	990	982	983	975	$\nu_{s}CN$
				970				
826	813	805	810	810	804	810	810	CH_3 rock
		394	409	386		392	392	ν(M-Cl) and ν(M-N)
		353		358		373		
					335		340	
			325	317	315			
		260	298	286	283	274		
						234	228	
		185		204			192	

We propose a similar mechanism as invoked by Kiesel and Schram, for the reactions of NMe_3 with the tervalent metal halides, MCl_3(M=Ti, V and Cr).



The intermediate complex, $[MCl_3(NMe_3)]$, may undergo further reaction(a) via addition of a further ligand molecule or (b) via elimination of $Cl^{\bullet}$ to give the reduced M(II) species. Alternatively, it may immediately precipitate (c). Specifically for vanadium, the latter occurs and the mono-adduct, $[VCl_3(NMe_3)]$ is obtained, in comparable yield to the vanadium (III) bis-adduct. It has been shown that the tervalent bis-adducts, $[MCl_3(NMe_3)_2]$ (M=Ti, V and Cr) all loose amine in benzene solution, at varying rates, giving the binuclear species $M_2Cl_6(NMe_3)_3$. These binuclear complexes cannot be readily reconverted to the monomeric five-coordinate bis-adducts. Similarly, we have found that once $[VCl_3(NMe_3)]$ precipitates it does not react further with excess NMe_3. The type of structure envisaged for the mono-adduct is a halogen bridged polymer, based on octahedral vanadium (III),(C).



C

No mention of a species such as $VCl_3(NMe_3)$ is made in the work of Kiesel and Schram, which is perhaps surprising since it was a proposed intermediate in the reaction scheme.

$$VCl_4 + NMe_3 \dashrightarrow VCl_4(NMe_3) \longrightarrow VCl_3(NMe_3) + Cl^{\bullet}$$

In their work, no insoluble vanadium products were obtained with an excess of NMe_3. With a deficiency of amine

($VCl_4:NMe_3$, 1:1.5), no $VCl_3(NMe_3)_2$ was formed, and the light red product mixture was not characterized. From their proposed reaction scheme, this product mixture should contain some [$VCl_3(NMe_3)$].

$$VCl_4 + NMe_3 \longrightarrow VCl_4(NMe_3) \longrightarrow VCl_3(NMe_3) + Cl^{\bullet}$$

$$Cl^{\bullet} + NMe_3 \longrightarrow Me_2NCH_2^{\bullet} + HCl$$

$$HCl + VCl_4(NMe_3) \longrightarrow VCl_3(NMe_3) + Me_2NCH_2^{+}Cl^{-}$$

The infra-red evidence indicated that the Cl^- from $Me_2NCH_2^+Cl^-$ was in fact associated with a larger anionic species. We have compared their reported infra-red data with other fully characterized products of this system (Table 4.2) and can find no evidence for the presence of [$VCl_3(NMe_3)$]. Instead, we propose an anion of the type $[V_2Cl_7(NMe_3)_2]^-$, analogous to $[V_2Cl_9]^{3-}$ and $[V_2Cl_6(NMe_3)_3]$, is present in the amine deficient product. For comparison $[V_2Cl_9]^{3-}\cdot3[Et_2NH_2]^+$ exhibits low infra-red bands a 313(s) and 260(m) cm^{-1}, with associated shoulders at 350 and 290 cm^{-1}.[310]

With titanium (III) and chromium (III) we isolated the divalent species [$MCl_2(NMe_3)$] (M=Ti and Cr). The major product of the reaction is clearly the tervalent bis-adduct $MCl_3(NMe_3)_2$, there is no evidence for $MCl_3(NMe_3)$. The yield of $MCl_2(NMe_3)$ is low, showing that reaction (b) is of secondary importance with respect to formation of [$MCl_3(NMe_3)_2$] (a).

Table 4.2 Infra-red spectral data of the various products found in the VCl_4/NMe_3 and VCl_3/NMe_3 systems (cm^{-1}).

$VCl_3(NMe_3)_2$ VCl_4 or VCl_3:NMe_3 1:xs	$VCl_3(NMe_3)$ VCl_3:NMe_3 1:xs	Light red product VCl_4:NMe_3 1:1.5	$Me_2N{=}CH_2^+Cl_2^-$	$V_2Cl_6(NMe_3)_3$
	3130(s)	3120(vs)	3080(m)	3090(s)
3013(s)	3015(m)	3023(s)	3013(sh)	3025(sh)
2982(s)	2950(m)	2983(m)	2988(m)	2950(w)
2932(s)		2925(sh)	2910(sh)	2920(w)
2905(s)				
2880(m)				
2855(s)		2860(m)		2854(w)
2824(m)				2830(sh)
2796(ms)	2710(w,sh)	2790(m,br)		2780(w)
	2640(m,br)			
		1696(m)	1678(m)	

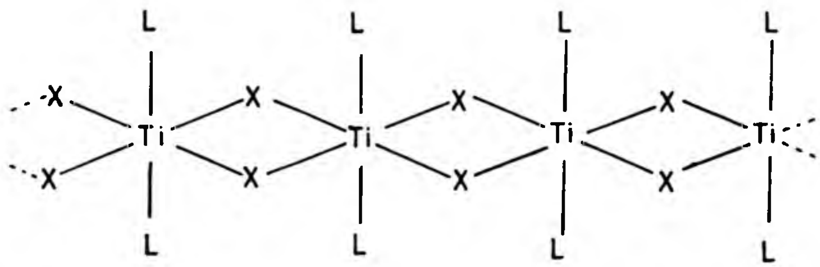
Table 4.2 continued.

		1606(w,br)		
			1498(m)	
			1491(m)	
1478(vs)		1478(s)		1478(s)
1458(vs)	1465(s)	1465(s)	1464(m)	1462(s)
	1445(s)	1450(s)	1450(ms)	
1404(vs)	1410(w)	1412(ms)		1406(m)
	1380(s)	1379(m)	1381(m)	1372(m)
			1333(m)	
1238(m)	1255(m)	1250(mw)		1251(m)
			1172(vs)	
1103(ms)	1100(w)			1090(m)
	1045(m)	1050(mw)	1078(s)	1040(w)
				1012(m)

Table 4.2 continued.

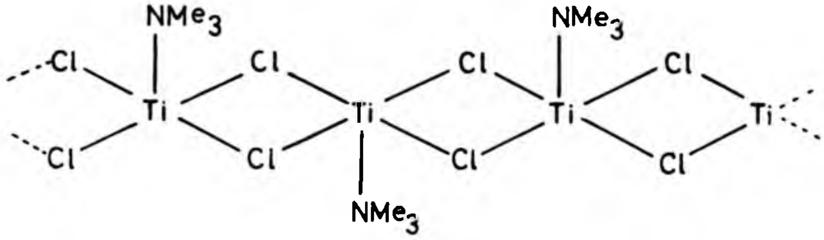
987(vs)	990(s)	980(s)	992(vs)	982(s)
	970(s)	975(sh)		
	845(m)			
812(vs)	810(m)	811(mw)		804(m)
	720(m)	719(w)	720(w)	720(m)
506(s)		490(w)	500(s)	520(w,br)
442(s)				448(m)
		423(m)	430(s)	422(sh)
410(vs)				
	386(m)			
	358(vs)		345(w)	335(s)
	317(vs,br)	320(vs,br)		315(s)
289(m)	286(s)		280(w,sh)	283(m)
252(m)		255(ms)		
	204(s,br)			

The chemistry of titanium (II) has been little investigated, presumably because of the difficulty in handling these strongly reducing species. Titanium (II) halides are polymeric, and undergo addition reactions even less readily than titanium (III) halides. Direct reaction of acetonitrile does yield $TiX_2(MeCN)_2$ (X=Cl and Br), which readily gives ligand substitution products with a number of other donors.[311,312] All the products reported were considered to be halogen-bridged polymers in the solid state (D).



D

Similarly, we propose that our complex also has a polymeric structure, eg (E).



E

Although the chemistry of chromium (II) is more extensive than that of titanium (II), there is still scant knowledge of the coordination behaviour of the CrX_2(X=Cl, Br and I) series. These chromium (II) halides, also, react with acetonitrile[313] and with pyridine,[314] giving 1:2 adducts. In the cases of $[CrX_2L_2]$ (X=Cl and Br, L=MeCN and py) polymeric, halogen bridged octahedral structures, analogous to (D), were proposed For our complex, $[CrCl_2(NMe_3)]$, we suggest a similar polymeric structure, as previously described for the analogous titanium (II) complex (E). Chromium (II) complexes are labile in contrast to chromium (III) species which are, characteristically, kinetically inert. Consequently Cr (II) complexes may be used to accelerate reactions of Cr (III) species. The Cr (II) species are often produced by the addition of zinc dust, eg in the preparation of $[CrCl_3(T.H.F.)_3]$[290]. The zinc is thought to fix to the surface of the $CrCl_3$ via halogen bridging, electron transfer then occurs giving labile, soluble Cr(II) ions. Further reaction may occur involving the Cr(II) species binding to the $CrCl_3$ surface via halogen bonding.[315,316] Addition of zinc dust is recommended in the preparation of $CrCl_3(NMe_3)_2$ from $CrCl_3$ and neat NMe_3 [295] We found, however that the zinc was not vital, although without it the reaction was much slower. Of two systems sealed at the same time, the one with zinc dust included gave the characteristic blue-purple solution within six hours whereas the one without took two weeks to achieve the same result. Neither the titanium (III) or vanadium (III) systems needed zinc dust, being d^1 and d^2 systems respectively.

CHAPTER FIVE.

REACTIONS OF HEXAMETHYLDISILOXANE AND HEXAMETHYLDISILATHIANE

WITH

COVALENT TRANSITION METAL HALIDES.

INTRODUCTION

It has recently been shown,[317] in this laboratory, that titanium (IV) chloride and tris(trimethylsilyl) amine react to give trimethylchlorosilane and catena-di-μ-chloro bis-μ-(trimethylsilylamino) di (chlorotitanium (IV)) :-

$$2TiCl_4 + 2N(SiMe_3)_3 \longrightarrow 4Me_3SiCl + \frac{1}{n}[(Cl_2TiNSiMe_3)_2]_n$$

The latter features planar dimeric (Ti-N) units polymerised via chlorine bridges[318,319] (Fig 5.1), and is the first confirmed example of a ring of this type. There are very few examples of transition metal containing heterocycles of the type $(-M-Y)_n$, where Y=O,N,P,S etc, other than those formed via coordination [107]. Apart from the example above the only other titanium heterocycle confirmed by crystal structure data, is the tetrameric ring $[(C_5H_5)TiCl(O)]_4$[320,321] (Fig 5.2). This compound contains an eight membered (Ti-O) ring, with tetrahedral titanium atoms and Ti-O-Ti bonds distorted from linearity. It may be prepared by careful hydrolysis of $(C_5H_5)TiCl_3$[322]:-

$$4(C_5H_5)TiCl_3 \xrightarrow[-4HCl]{+2H_2O} 2[(C_5H_5)TiCl_2]_2O$$

$$\xrightarrow[-4HCl]{+2H_2O} [(C_5H_5)TiCl(O)]_4$$

or by reaction with dry acetone under anaerobic conditions.[323] This is the only such compound to have the presence of a (Ti-O) ring confirmed by on x-ray determination. There are many more reports in which such rings have been suggested on the

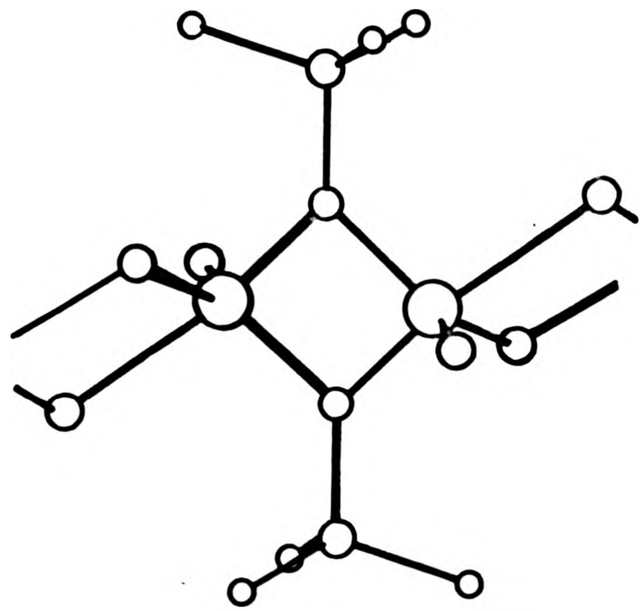


FIGURE 5.1 $[Cl_2Ti(NSiMe_3)]_2$: one unit of the ordered chain

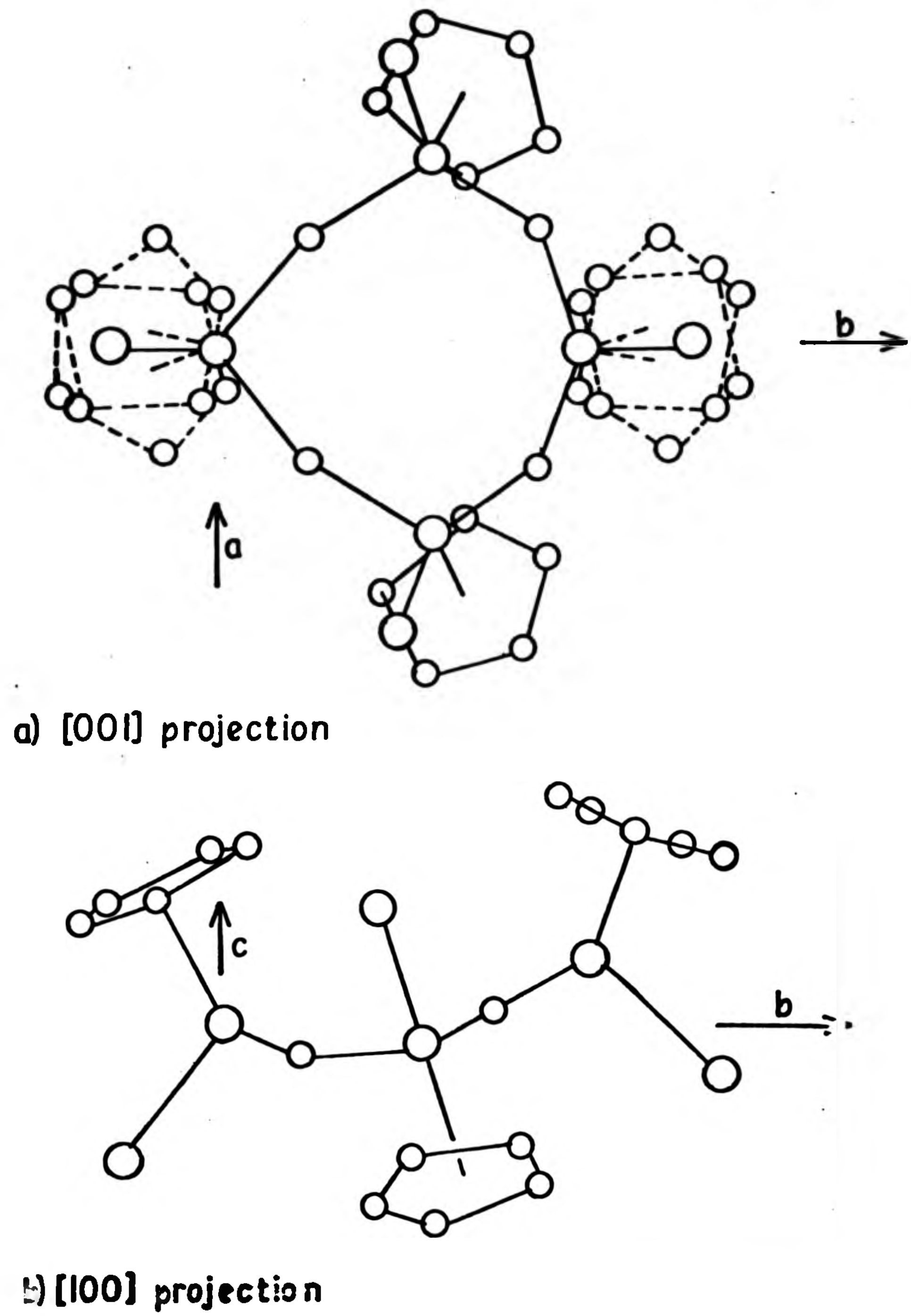


FIGURE 5.2 Structure of $[(h^5C_5H_5)TiClO]_4$

basis of chemical analysis and molecular weight data.[324-327]

There are no authenticated examples of rings of alternate titanium-sulphur atoms, the various titanium sulphides tend to have polymeric structures. The reactions of sodium and ammonium polysulphides with $(C_5H_5)_2TiCl_2$[328], and the reaction of elemental sulphur on $(C_5H_5)_2Ti(CO)_2$,[329] all result in the formation of a six-membered (TiS_5) heterocycle. The pentasulphide fragment functions as a bidentate ligand in occupying two metal coordination sites with the centroids of the two cyclopentadienyl rings completing a distorted tetrahedral coordination around the titanium atom (Fig 5.3)[329,330]. Attempted formation of smaller rings failed, in all cases $(C_5H_5)_2TiS_5$ was obtained.[331] Even reaction of $(C_5H_5)_2Ti(SH)_2$ with iodine only resulted in the formation of the titanium pentasulphide and $(C_5H_5)_2TiI_2$.

The vanadium pentasulphide $(C_5H_5)_2VS_5$ has been obtained similarly and shown to have the same structure as its titanium analog.[330] Another example of a transition metal containing (MS_5) rings is $[(NH_4)_2PtS_{15}].2H_2O$, the structure of which shows the presence of three six-membered rings by the coordination of three bidentate pentasulphide fragments (A).[332]

In contrast, reaction of $(C_5H_5)_2MCl_2$(M=Mo,W) with ammonium polysulphides results in the formation of a five-membered (MS_4) ring.[333] Here the MS_4 is non-planar but symmetrically placed with respect to the cyclopentadienyl rings[334]. (Fig 5.4)

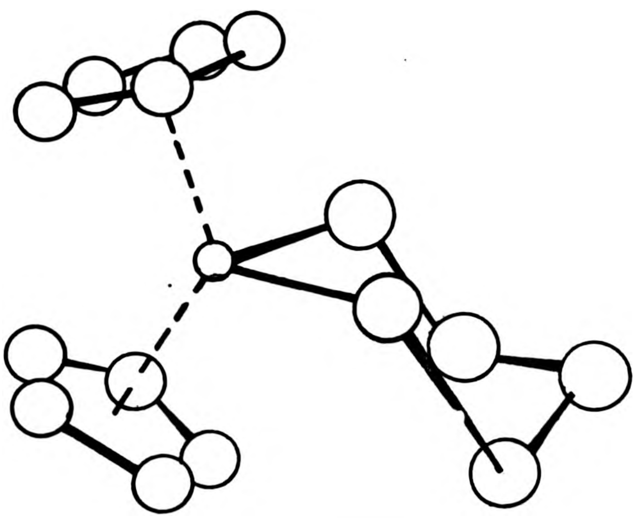


Fig. 5.3. Molecular configuration of

$[(h^5C_5H_5)_2TiS_5]$

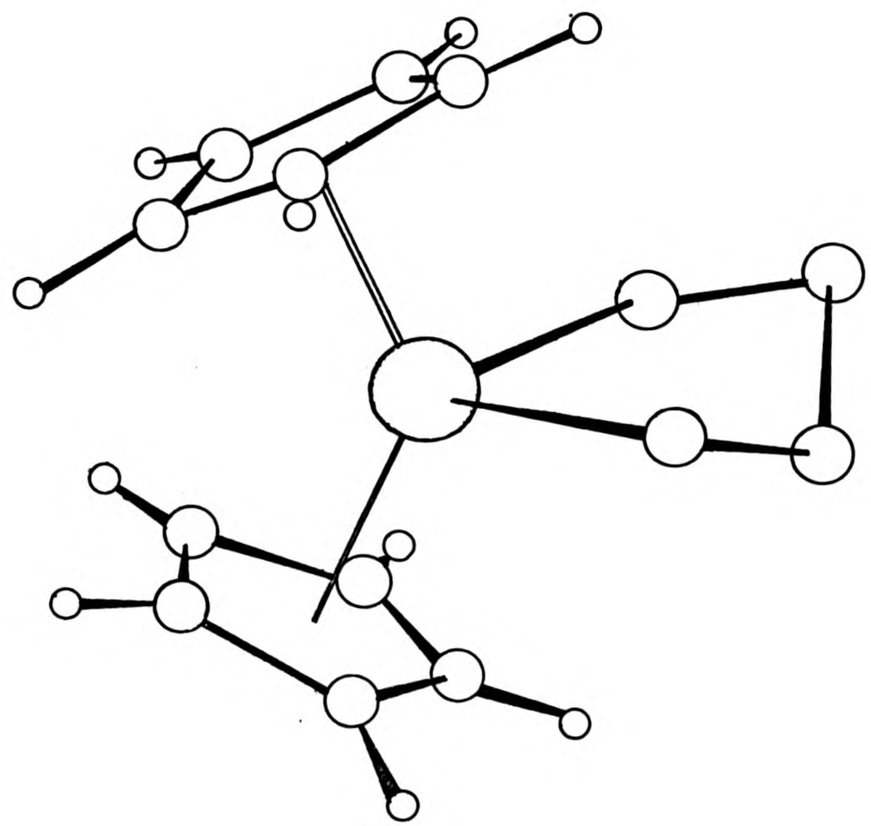
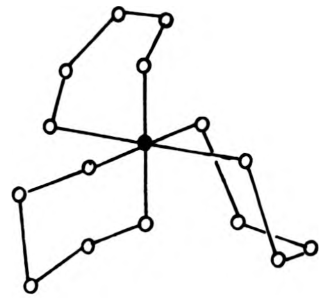


Fig.5.4 Structure of $(h^5C_5H_5)_2WS_4$



A

The general scarcity of transition metal heterocycles is in contrast to the main group elements, for which heterocyclic compounds are legion[107] (Table 5.1).

Hexamethyldisiloxane and hexamethyldisilathiane are both potential σ-donors and yet no such complexes have been prepared. For $(Me_3Si)_2O$ the $Si\hat{O}Si$ bond angle of 148° implies that both lone pairs are delocalized to some extent,[335] for comparison the $C\text{-}\hat{O}\text{-}C$ bond angle in dimethylether is 111°. Consequently it is a much weaker electron donor than that of an aliphatic ether. This is a well known feature of siloxanes [336] (Table 5.2) and is attributed to interaction of the filled oxygen p-orbitals with the empty silicon 3d-orbitals.[338-340]

Table 5.2 Geometrical parameters for the disiloxanes $(R_3Si)_2O$ (R=H,Cl,F,Ph and Me).

R	$Si\hat{O}Si$ Bond angle	(Si-O) Bond distance
H	144	1.634
Cl	146	1.592
F	156	1.580
Ph	180	1.616
Me	14[illegible]	

Table 5.1 Some heterocyclic rings $(M\text{-}X)_n$ (M=main group element, X=O or S).

Heterocycle	Examples and Remarks
$(RBO)_3$	A wide variety of substituted inorganic and organic derivatives known. Planar $(B\text{-}O)_3$ ring.
$(RBS)_2$	Only limited examples.
$(RBS)_3$	More favoured than $(RBS)_2$, large number of examples known. The ring is planar in $(BrBS)_3$.
$(R_2SiO)_n$	$3<n>25$. Extremely numerous. $(SiO)_3$ rings are generally planar, $(SiO)_4$ are puckered.
$(R_2SiS)_2$	Various derivatives known. In $(Me_2SiS)_2$ the ring is planar.
$(R_2SiS)_3$	Various examples. Relative yields of $(R_2SiS)_n$ (n=2,3) depends on reaction conditions. $(Me_2SiS)_3$ ring is puckered.
$(R_2GeO)_n$	n=3,4, various substituents. Less common than analogous silicon compounds.
$(R_2GeS)_n$	n=2,3 various derivatives.
$(R_2SnO)_n$	No confirmed examples.
$(R_2SnS)_2$	Rare, $(Bu^t_2SnS)_2$ recently synthesised and shown to be planar.[337]
$(R_2SnS)_3$	Fairly common. R=Ph and Me contains puckered $(SnS)_3$ rings.
$(R_2PbX)_n$	X=O,S. No confirmed examples.

For $(Me_3Si)_2S$, infra-red and Raman spectral studies indicate a bond order of 1.00 and a $Si\hat{S}Si$ bond angle of 104° suggesting that (p-d)π bonding is less important in the Si-S bond.[341] Both the Si-O and the Si-S bonds are readily cleaved by a variety of reagents. Reaction of $(Me_3Si)_2O$ with a variety of metal and non-metal halides gave the corresponding trimethylhalogenosilane and either trimethylsiloxy derivatives or the oxides,[340] for example:-

$$3(Me_3Si)_2O + 2BBr_3 \longrightarrow 6Me_3SiBr + B_2O_3$$

$$(Me_3Si)_2O + AlCl_3 \longrightarrow 2Me_3SiCl + (AlOCl)$$

Both of these examples are believed to proceed via an unstable addition compound:-

$$(Me_3Si)_2O + BBr_3 \longrightarrow (Me_3Si)_2\overset{+}{O}-\overset{-}{B}Br_3$$

$$(Me_3Si)_2\overset{+}{O}-\overset{-}{B}Br_3 \longrightarrow Me_3SiOBBr_2 + Me_3SiBr$$

On heating the reaction mixture, the final products are obtained:-

$$Me_3SiOBBr_2 \longrightarrow Me_3SiBr + BBrO$$

$$3BBrO \longrightarrow B_2O_3 + BBr_3$$

Cleavage also occurs on reaction with organometallic reagents, alcohols, hydrogen chloride etc, and a review of some typical reactions of $(Me_3Si)_2O$ is given in Fig 5.5.

Hexamethyldisilathiane is readily hydrolysed:-

$$(Me_3Si)_2S + H_2O \longrightarrow 2Me_3SiOH + H_2S$$

and similarly with alcohols:-

$$(Me_3Si)_2S + 2ROH \longrightarrow 2Me_3SiOR + H_2S$$

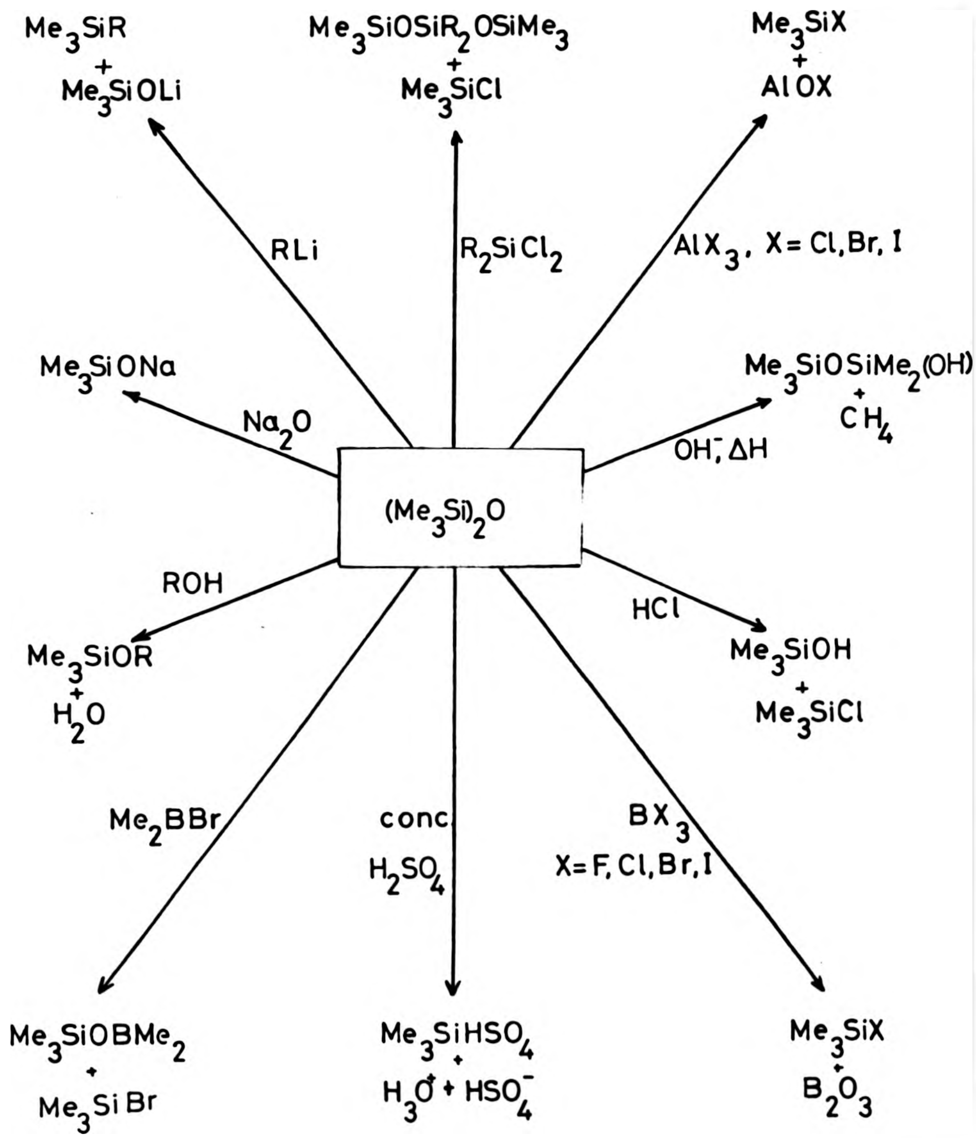


Fig. 5.5 Some typical reactions of hexamethyldisiloxane.

A similar pattern of behaviour to $(Me_3Si)_2O$ has been observed (Fig 5.6), indicating the weakness of the Si-Y(Y=O,S) bonds relative to Si-X (X=halogen) bonds,[342,343] eg:-

$$3(Me_3Si)_2S + BCl_3 \longrightarrow (Me_3SiS)_3B + 3Me_3SiCl$$

$$(Me_3SiS)_3B + BCl_3 \xrightarrow{heat} B_2S_3 + 3Me_3SiCl$$

With metal halides, Me_3SiX and the corresponding metal sulphide are obtained:-[344]

$$HgCl_2 + (Me_3Si)_2S \longrightarrow HgS + 2Me_3SiCl$$

$$CdCl_2 + (Me_3Si)_2S \longrightarrow CdS + 2Me_3SiCl$$

The lability of the Si-S bond has been exploited as a means of preparing sulphur containing complexes,[342,344,345] for example in the preparation of $[Ni(SMe)_2]_6$:-

$$Me_3SiSMe_3 + NiCl_2 \rightarrow [Ni(SMe)_2]_6 + [Ni(SMe_2)_2]_n + Me_3SiCl$$

As a natural extension of the chemistry of $(Me_3Si)_2O$ and $(Me_3Si)_2S$ we have studied their reactions with representative transition metal halides. We were particularly interested in preparation of novel heterocyclic compounds by analogous routes to that used in preparing the previously mentioned ring $[(Cl_2TiNSiMe_3)_2]_n$:-

$$(Me_3Si)_2Y + TiCl_4 \longrightarrow \frac{1}{n}[Cl_2TiY]_n + 2Me_3SiCl$$

$$Y=O,S$$

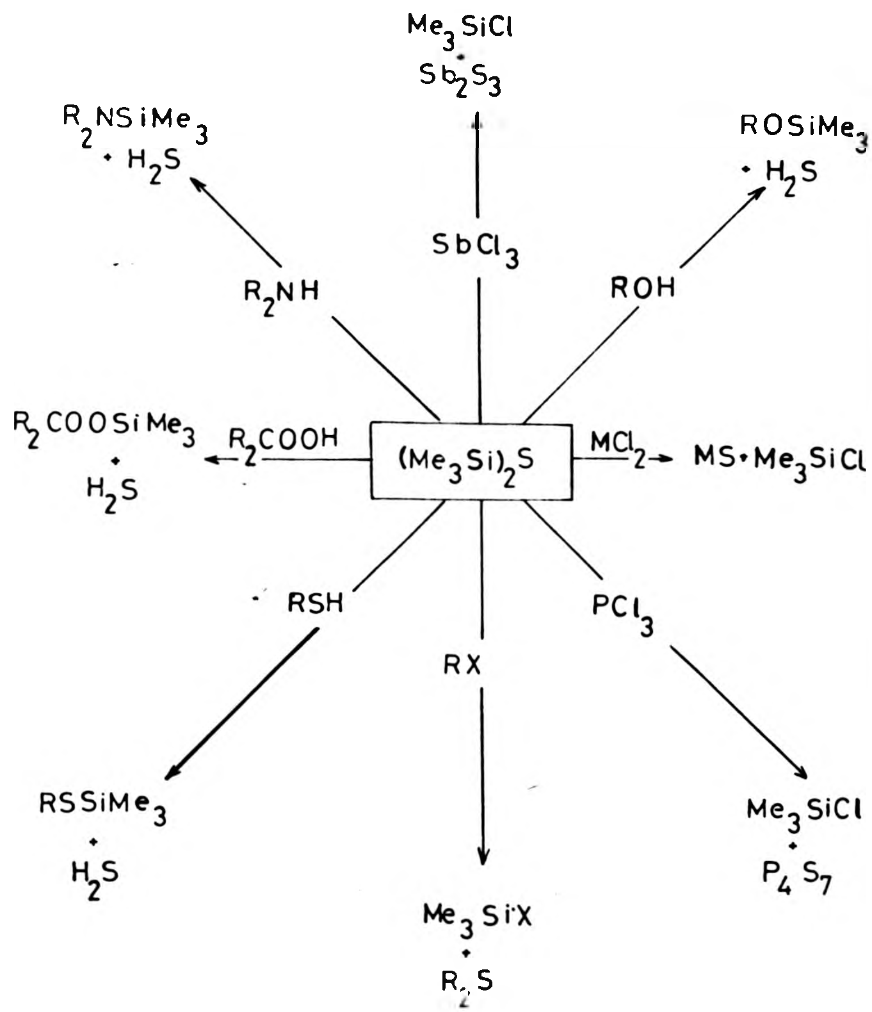


Fig. 5.6. Some typical reactions of hexamethyldisilathiane.

EXPERIMENTAL

5A Reactions of hexamethyldisiloxane :-

5Ai With titanium (IV) chloride.

a) ^{1}H.N.M.R. Study

$TiCl_4 + (Me_3Si)_2O$: $TiCl_4$ (1cm^3; 9.10mmols) and $(Me_3Si)_2O$ (1.9cm^3; 8.94mmols) were mixed in a dry N.M.R. tube, which was then sealed under nitrogen. ^{1}H.N.M.R. spectra were recorded at suitable time intervals (Table 5.3)

Table 5.3 ^{1}H.N.M.R. spectral data for a 1:1 mixture of $TiCl_4$ and $(Me_3Si)_2O$.

Time after mixing (mins)	$\frac{\text{Intensity of peak at } 0.065\ \delta \text{ppm}}{\text{Intensity of peak at } 0.398\ \delta \text{ppm}}$
4	5.88
6	4.15
8	1.56
10	0.63
12	0.17
15	∞

$TiCl_4 + 2(Me_3Si)_2O$: As above using a mixture of $TiCl_4$ (0.5cm^3,4.55mmols) and $(Me_3Si)_2O$ (1.9cm^3,8.94mmols) (Table 5.4).

$TiCl_4 + 4(Me_3Si)_2O$: As above using a mixture of $TiCl_4$ (0.5cm^3; 4.55mmols) and $(Me_3Si)_2O$(3.8cm^3; 17.88mmols). (Table 5.5)

Table 5.4 ^{1}H.N.M.R. spectral data for a 1:2 mixture of $TiCl_4$ and $(Me_3Si)_2O$.

Time (mins)	0.326 ppm peak intensity / 0.065 ppm peak intensity	0.412 ppm peak intensity / 0.065 ppm peak intensity
15	0.16	
25	0.93	
40	0.41	1.31
50	0.56	1.40
58	0.79	1.19
65	0.97	1.16
75	1.15	1.19
85	1.18	1.44
100	1.26	1.56
130	1.39	1.92
155	1.52	2.11
2590	2.56	2.78
1 month	4.34	2.30
At completion	0	3.17

b) $TiCl_4$ + $(Me_3Si)_2O$: $TiCl_4$(cm^3; 27.30mmols) and $(Me_3Si)_2O$ (5.7cm^3; 26.82mmols) were mixed in a 25cm^3 round bottomed flask then fractionally distilled under 1 atmosphere of nitrogen. Three fractions were obtained:-

i) A colourless liquid, boiling point 332K. Shown, by comparison of ^{1}H.N.M.R, infra-red and bpt. data with that of an authentic sample, to be Me_3SiCl.

Table 5.5 [1]H.N.M.R. spectral data for a 1:4 mixture of $TiCl_4$ and $(Me_3Si)_2O$.

Time (mins)	0.326 δ ppm peak intensity / 0.065 δ ppm peak intensity	0.412 δ ppm peak intensity / 0.065 δ ppm peak intensity
30	0.01	
90	0.14	
240	0.45	
345	0.52	
420	0.29	0.31
645	0.30	0.38
1500	0.46	0.57
1680	0.46	0.52
1860	0.52	0.66
2820	0.52	0.62
7140	0.54	0.49
10 days	0.61	0.52
2 months	0.32	0.76
At completion	0	0.52

ii) A colourless liquid (I), bpt. 433-453K. Exhibited positive chloride and titanium tests.

Infra-red Data (cm^{-1}; neat liquid) 2950(m) 2890(w) 1445(w) 1405(w) 1325(vw) 1255(vs) 950(vs) 835(vs) 765(s) 635(s) 475(vs) 370(s) 300(m)

[1]H.N.M.R. Data (δppm; ref TMS; neat liquid) 0.37

iii) Blue-black intractable residue. Insoluble in conc. HCl, H_2SO_4 and HNO_3.

c) <u>$TiCl_4$ + $2(Me_3Si)_2O$:</u> $TiCl_4$ (3.9cm^3;35.49mmols) and $(Me_3Si)_2O$(15cm^3,70.57mmols) were mixed in a 100cm^3 capacity ampoule, degassed at 96K and sealed under vacuum. On warming to R.T. a yellow colour was observed which rapidly disappears to leave a clear, colourless solution. After ~1 month precipitation of a white solid (II) slowly started, which was deemed complete after a further month. The volatile products were removed by distillation under reduced pressure. The white solid was washed thoroughly with benzene and hexane, then pumped dry (4.63g; 69.4%). Small samples of the white solid (~0.5g) were sealed in ampoules containing either DMF, DMSO, THF, MeCN or dioxan, and kept at 323K. Samples were also extracted in a soxhlet with boiling THF, MeCN and dioxan. No solubility or reaction with any of these donor solvents was observed.

<u>White Solid (II)</u>

<u>Infra-red Data</u> (cm^{-1}; nujol and H.C.B.mulls) 2970(m) 2930(w) 2895(w) 1450(w) 1410(w) 1330(vw) 1260(s) 1250(s) 985(vs) 950(m) 852(vs) 755(s) 655(vw) 153(s)

After exposure to air (cm^{-1}; nujol and H.C.B.mulls) 3610(m,br) 3400-3160(m) 2960(m) 2930(w,sh) 2900(w,sh) 2850(w,sh) 1445(w,br) 1405(w) 1260(s) 1255(s,sh) 1240(s) 1015(w) 940(vs) 910(s) 845(vs) 800(w) 760(m,sh) 750(s) 730(m,sh) 630(w,sh) 580(s) 440(vs) 400(m,sh) 375(w,sh) 315(vw,br) 290(w)

Chemical Analysis (%) Found C:20.51, H:4.72, Cl:19.21, Calc'd for $C_3H_9ClO_2SiTi$, C:19.11 H:4.81, Cl:18.80.

Melting Point >523K.

5Aii With bis(cyclopentadienyl) titanium (IV) chloride.

$(C_5H_5)_2TiCl_2$ (0.75g; 3.01mmols) and $(Me_3Si)_2O$ (0.8cm^3; 3.76mmols) were placed in a ~250cm^3 capacity round bottomed flask containing ~150cm^3 benzene. The reaction mixture was then heated under reflux in a nitrogen atmosphere for ~90hrs. No visible change was observed and unreacted $(C_5H_5)_2TiCl_2$(0.72g;96%) was recovered.

5Aiii With zirconium (IV) bis(acetonitrile).

$ZrCl_4$(3.33g;14.29mmols), dissolved in ~50cm^3 MeCN and the solution filtered into a ~100 cm^3 capacity ampoule containing $(Me_3Si)_2O$(6.0cm^3; 28.21mmols). The solution was degassed at 96K and sealed under vacuum. On warming to R.T. a colourless solution developed, no visible change occured on storing at 323K for a week. Removal of solvent followed by washing with hexane gave a white solid (III) (4.52g;96.5%) which was soluble in benzene, $CHCl_3$ and MeCN.

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2970(s) 2920(s) 2860(w,sh) 2780(w,sh) 2400(s) 2378(vs) 2340(m,sh) 1640(w) 1585(w) 1540(w) 1475(s) 1400(m,br) 1357(m) 1210(m) 1110(w) 1020(s) 995(m,sh) 940(s) 915(m,sh) 890(m) 830(m) 740(m) 680(s,sh) 670(vs) 565(vs,br) 500(vs,br) 400(m,sh) 360(vs) 290(vs)

After exposure to air: (cm^{-1}; nujol and H.C.B. mulls)

3500-3040(vs) 2980(s) 2920(s) 2850(w,sh) 2310(s) 2280(vs) 2260(m) 1680(m,sh) 1600(s) 1430(m,sh) 1410(m) 1365(m) 1255(m) 1220(m) 1100(m) 940(m) 920(m) 890(w) 840(m) 750(m) 700(s,br) 620(s) 610(s) 505(m,br) 400(w,sh) 300(m,sh) 315(vs)

^{1}H.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$ solution)

1.904 (I) , - 0.032 (3)

Chemical Analysis (%) Found C:18.89, H:2.16, N:5.92, Cl: 34.04, MWT (Osmometric MeCN) : 828, Calc'd for $C_5H_{12}Cl_3ONSiZr$, C:18.32, H:3.39, N:4.27, Cl:32.45, MWT: 328 (monomer).

5Aiv With tin (IV) chloride.

$SnCl_4$(1cm^3;8.68mmols) and $(Me_3Si)_2O$ (7.4cm^3; 34.82mmols) were mixed in a ~50cm^3 capacity ampoule, degassed at 96K then sealed under vacuum. On storage at 323K, a white solid slowly deposited and sublimed to the neck of the ampoule. The white product was shown by ^{1}H.N.M.R. and i.r. spectroscopy to be $MeSnCl_3$.

5Av With chromium (III) chloride.

a) $CrCl_3$(1.72g;10.83mmols) and $(Me_3Si)_2O$ (8cm^3;37.64mmols) were placed in a ~50cm^3 capacity ampoule, degassed at 96K, then sealed under vacuum. No reaction was observed on storage at 323K over a period of several months. $CrCl_3$ was recovered unchanged (1.72g;100%).

b) [$CrCl_3(THF)_3$] was prepared by soxhlet extraction of $CrCl_3$(1.23g;7.77mmols) with T.H.F. (~100cm^3). The resulting solution was transferred to an ampoule containing

$(Me_3Si)_2O$(5cm^3; 23.52mmols). The ampoule was degassed at 96K and sealed under vacuum. No reaction was observed on storage at 323K over several months and $[CrCl_3(THF)_3]$(2.97g;96%) was recovered unchanged.

5B Reactions of hexamethyldisilathiene:-

5Bi With titanium (IV) chloride.

a) $(Me_3Si)_2S$ (4cm^3;19.10mmols) and $TiCl_4$(2cm^3;18.2mmols) were each dissolved in ~100 cm^3 benzene, then slowly dripped together into a further ~100cm^3 benzene, cooled to 273K. Immediate reaction occured precipitating a dark brown solid (IV) which was collected by filtration, thoroughly washed with benzene and pumped dry (2.67g). 1.25g of the product was treated with ~50cm^3 MeCN, giving a red solution and an insoluble black residue (V). Removal of the insoluble solid followed by removal of solvent from the filtrate yielded an orange-red solid (VI) (1.83g81%). The orange-red product was insoluble in non-coordinating solvents but soluble with reaction in coordinating ones. 1.25g of dark brown solid (IV) were treated with T.H.F. in a similar fashion and a red solid (VII) isolated.

Dark Brown Solid (IV)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 800(m) 725(s) 560(w,br) 300(vw,br) 198(s,br)

Chemical Analysis (%) Found S:25.28 Calc'd for Ti_2S, S:25.10 .

Orange-red acetonitrile complex (VI)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2945(w) 2920(m) 2840(w) 2305(m) 2280(m) 2242(w,sh) 1734(m)

1670(m) 1570(m) 1400(m) 1360(m) 1295(m) 1257(m)

1210(m) 1085(s) 932(m,sh) 880(s,br) 840(s,br) 750(s,br)

720(m,sh) 615(m) 545(vs) 485(w) 400(m,sh) 363(s) 325(vs)

270(w) 195(m)

<u>^{1}H.N.M.R. Data</u> (δ ppm; ref TMS; d^3MeCN solution) 2.08 (singlet)

<u>Chemical Analysis</u> (%) Found C:26.80, H:3.86, N:15.00, Cl:25.46, M.T(Osmometric in MeCN) :291, Calc'd for $C_6H_9N_3Cl_2STi$, C:26.30, H:3.31, N:15.33, Cl:25.88, M.T:274.

<u>Orange tetrahydrofuran complex (VII)</u>

<u>Infra-red Data</u> (cm^{-1}; nujol and H.C.B. mulls) 2950(s)

2860(s) 1640(w) 1445(s) 1410(w) 1362(m) 1342(m) 1300(m)

1255(vs) 1170(w) 1090(vs,sh) 1072(vs) 1038(vs) 1015(vs)

915(m) 840(vs) 720(vs) 665(m) 540(m) 365(vs,br) 325(vs,br)

272(w) 198(m)

<u>^{1}H.N.M.R. Data</u> (δ ppm; ref TMS; d^3MeCN solution) 1.49(1), 1.74(2), 3.35(1) 3.58(2)

<u>Chemical Analysis</u> (%) Found C:39.06, H:6.71, Cl:19.05, Calc'd for $C_{12}H_{24}O_3Cl_2STi$, C:39.25, H:6.59, Cl:19.31.

b) $TiCl_4$ ($2cm^3$;18.2mmols) was dissolved in benzene ($\sim 100cm^3$) then MeCN(1.50g;36.54mmols) slowly added to give $[TiCl_4(MeCN)_2]$ as a slurry in benzene.$(Me_3Si)_2S$ ($4cm^3$, 19.1 mmols), dissolved in benzene ($\sim 150cm^3$), was slowly dripped onto this slurry. The orange precipitate formed initially turned dark brown overnight. The product (VIII) was collected by filtration, washed with benzene and pumped dry (4.09g,96%) Treatment of the brown solid with excess MeCN followed by removal of solvent gave a red solid shown by analysis and i.r.

data to be identical to (VI) prepared in (a).

Dark Brown Solid (VIII)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2950(vs) 2920(s) 2850(w) 2308(s) 2280(s) 1585(w,br) 1400(w) 1355(m) 1020(m) 943(m) 840(w) 550(w) 400(s,sh) 376(s) 320(m,sh)

^{1}H.N.M.R. Data (δppm; ref TMS; d^5 pyridine solution) 1.98

Chemical Analysis (a) Found, C:19.98, H:2.46, N:12.62, Cl:30.52, Calc'd for $C_4H_6N_2Cl_2STi$, C:20.62, H:2.60, N:12.02, Cl:30.44.

c) $TiCl_4$ ($1cm^3$;9.10mmols) was dissolved in ~100cm^3 MeCN, and $(Me_3Si)_2S$ in a further ~100cm^3 MeCN. The two solutions were dripped into a flask containing a further ~100cm^3 MeCN. After complete addition of the reactions the mixture was heated at reflux for ~15 hours. A fine precipitate formed on heating, and a yellow solid (IX) was obtained on removal of solvent.

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2980(m) 2930(s) 2310(m) 2260(w) 1715(m) 1640(m) 1550(m) 1480(m) 1405(s) 1365(m) 1285(w) 1255(m) 1220(w) 1100(m) 1040(s) 985(m) 935(m) 890(m) 840(m) 800(m) 760(m) 720(m) 620(m) 540(m) 540(m) 490(m) 370(s,br) 340(s,br) 285(s,br)

^{1}H.N.M.R. Data (δppm; ref TMS; d^3MeCN solution) 2.194 (d^5 pyridine solution) 2.409(1) 2.167(3.5) 1.940(3.5)

5Bii With bis (cyclopentadienyl) titanium (IV) chloride.

As in 5Aii

5Biii With zirconium (IV) chloride bis(acetonitrile).

$ZrCl_4$(2.83g;12.18mmols) was dissolved in MeCN (~100cm^3) and $(Me_3Si)_2S$(2.95cm^3;12.18mmols) slowly added. The ampoule was degassed and sealed under vacuum at 96K, a bright yellow solution developed on warming to R.T. and after ~3 hours at 323K a bright orange solid had formed. The orange product (X) was collected by filtration, washed thoroughly with MeCN and pumped dry. The solid was insoluble in most common organic solvents but showed slight solubility in $CHCl_3$.

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2960(m) 2920(m) 2305(s) 2280(vs) 1630(w). 1580(w) 1475(m) 1400(m) 1355(m) 1260(s) 1087(m) 1031(s) 940(s) 900(m) 845(m) 795(m,sh) 765(s) 685(s) 610(m) 575(m) 400(m) 365(s) 320(vs,br) 305(s,sh) 260(vs,br)

^{1}H.N.M.R. Data (δ ppm; ref TMS; $CDCl_3$ solution)
1.89(1) -0.04(2)

Chemical Analysis (%) Found C:12.97, H:1.59, N:5.21, Cl:6.56

5Biv With tin (IV) chloride.

$(Me_3Si)_2S$(4cm^3;16.52mmols) was added dropwise to a benzene (~150cm_3) solution of $SnCl_4$(2cm^3;17.35mmols). Immediate reaction occurred to precipitate a yellow solid which darkened to a mustard yellow colour on stirring overnight. The product (XI) was collected by filtration, washed with benzene and hexane, then pumped dry (3.16g;82%). The mustard solid was insoluble in all common organic solvents and showed no reaction with either DMF, THF, DMSO or MeCN on prolonged contact at 323K.

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 1270(m) 1090(m,br) 1040(s,br) 805(s) 730(vw) 350(vw) 325(s) 360(vs)

Chemical Analysis (%) Found, Cl:31.74, S:15.06 Calc'd for Cl_2SnS, Cl:32.00, S:14.47.

5Bv with dimethyl tin (IV) chloride.

Me_2SnCl_2 (5.01g;22.81mmols) and $(Me_3Si)_2S$ (5.50cm^3; 22.71mmols), both dissolved in ~100cm^3 benzene were slowly added together at 273K. On stirring overnight at R.T. a small quantity of white solid precipitated, further precipitation occurred over ~10 days. The product was collected by filtration and shown by i.r. and ^{1}H.N.M.R. data to be cyclo-tris(dimethylstannothiane).

5Bvi With titanium (III) chloride tris (tetrahydrofuran).

$(Me_3Si)_2S$ (1.45cm^3;5.99mmols), diluted with 25cm^3 THF was slowly dripped into a THF solution of $TiCl_3$(0.92g;5.96mmols). The reaction vessel was evacuated and sealed at 96K, on warming to 323K a grey precipitate and solution developed. The grey solid (XII) was collected by filtration, washed with hexane and pumped dry (0.83g; 62%). The product was slightly soluble in polar solvents such as THF, $CHCl_3$, CH_2Cl_2 and MeCN but decomposed rapidly in solution leaving white or grey precipitates.

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2995(m,sh) 2975(s,sh) 2950(s) 2935(s,sh) 2898(s) 2870(s,sh) 1445(m) 1338(m) 1292(w) 1255(m) 1130(m) 1080(m,br) 1035(s)

1005(vs) 955(w) 920(m) 865(m,sh) 845(vs) 835(vs) 800(m,sh) 718(w) 670(m) 355(vs) 325(vs) 295(s) 280(m,sh) 270(m)

Chemical Analysis (%) Found, C:32.50, H:5.51, Cl:18.33, Calc'd for $C_6H_{12}O_{1.5}ClSTi$, C:32.20, H:5.37, Cl:15.85

5Bvii With vanadium (III) chloride tris (tetrahydrofuran).

A mixture $(Me_3Si)_2S$ (1.6cm^3;6.6mmols), $[VCl_3(THF)_3]$ (2.50g;6.69mmols), and THF (~100cm^3) were placed in an ampoule which was then degassed and sealed at 96K. The black solid (XIII) which precipitated on warming to R.T. was collected by filtration, washed with THF and pumped dry (0.25g;17.7%). The product was in soluble in all the common organic solvents.

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 1255(m) 1080(m,br) 1035(m) 1005(s) 910(w) 840(s,br) 800(m,br)

Chemical Analysis (%) Found, V:24.2, S:57.9, (chloride analysis proved unreliable) Calc'd for $ClVS_4$, V:23.7, S:59.8.

5Bviii With chromium (III) chloride tris (tetrahydrofuran).

A mixture of $[CrCl_3(THF)_3]$ (4.11g;10.96mmols) dissolved in THF (~100cm^3) and $(Me_3Si)_2S$ (2.60cm^3;10.73mmols) was placed in an ampoule, which was then evacuated and sealed at 96K. On warming to 323K a dark brown solid (XIV) slowly formed, which was collected by filtration, washed with THF and hexane, then pumped dry (1.43g;58.5%). The product was slightly soluble in THF and DMSO.

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 2990(s) 2950(s,sh) 2915(m,sh) 2880(m) 1455(m) 1425(w) 1395(w) 1310(w) 1270(s,sh) 1260(s) 1175(w) 1105(s) 1080(s) 1030(m) 970(w) 875(vs) 755(m) 730(m,sh) 690(w) 660(w) 365(s,sh)

340(vs,br) 310(m) 285(w)

^{1}H.N.M.R. Data (δppm; ref TMS; d^6 DMSO solution)

3.595 (1) 1.759 (1)

Chemical Analysis (%) Found, C:28.30, H:4.47, Cl:15.50, S:13.23, Calc'd for $C_6H_{12}O_{1.5}ClCrS$, C:31.67, H:5.27, Cl:15.58, S:14.09.

DISCUSSION

5A Reactions of hexamethyldisiloxane:-

5Ai With titanium (IV) chloride.

Titanosiloxanes form an important section of silicon chemistry in general. Much discussion concerning synthetic methods and possible industrial uses has appeared in both the chemical journals and the patent literature.[340,346-349]

Tetrakis(trialkylsiloxy) titanium (IV) compounds can be easily prepared by a variety of routes but the most common are exemplified below:-

$$4Me_3SiOH + TiCl_4 \xrightarrow{NH_3} (Me_3SiO)_4Ti + 4NH_4Cl$$

$$4Et_3SiONa + TiCl_4 \longrightarrow (Et_3SiO)_4Ti + 4NaCl$$

$$4Ph_3SiOH + Ti(OBu^n)_4 \longrightarrow (Ph_3SiO)_4Ti + 4Bu^nOH$$

By controlling the stoichiometry of the reaction between trimethylsilanol and tetrakis(isopropoxy) titanium (IV), it is possible to prepare mono- and bis-(trimethylsiloxy) titanium (IV) alkoxides as well as the tetrakis (trimethylsiloxy) titanium (IV) compound.[350] A series of (trialkylsiloxy) titanium(IV) halides of the type $(R_3SiO)_nTiX_{(4-n)}$ (n=1,2,x=Cl,Br) have been obtained by reaction of hexaalkyldisiloxanes with titanium (IV) halides, in the presence of $AlCl_3$ as catalyst.[351,352] Further substitution was reported not to occur, unless $FeCl_3$ was used instead of $AlCl_3$, when complete cleavage of the disiloxane occurred, giving $(TiO_2)_n$. Yastrebov[353] calculated the three equilibrium constants for the sucessive replacement of chlorine atoms from $TiCl_4$ by (Me_3SiO) groups from $(Me_3Si)_2O$:-

$$(Me_3SiO)_{(i-1)}TiCl_{4-(i-1)} + (Me_3Si)_2O \xrightleftharpoons{Ki} Me_3SiCl + (Me_3SiO)_iTiCl_{(4-i)}$$

However since the information on the actual chemical species in these systems, suggested and/or involved, was scant we felt a further investigation was in order. In our study the reaction was conveniently studied by proton N.M.R. in three ratios $[TiCl_4] : [(Me_3Si)_2O]$ 1:1, 1:2 and 1:4.

Equimolar proportions of the reactants were directly mixed in an N.M.R. tube, and sealed. Spectra were recorded over a period of fifteen minutes (Fig 5.7) by which time the $(Me_3Si)_2O$ had been totally consumed. By reference to the spectra of known samples of $(Me_3Si)_2O$ (0.065 δ ppm) and Me_3SiCl (0.404 δppm), the high field signal, was assigned to $(Me_3Si)_2O$ and that at 0.398 δppm to Me_3SiCl. In the absence of the appearance of a third peak during the course of the reaction, it would seem that the initial product of the reaction, $[Me_3SiOTiCl_3]$, has the same chemical shift as Me_3SiCl.

$$TiCl_4 + (Me_3Si)_2O \longrightarrow Me_3SiOTiCl_3 + Me_3SiCl$$

A sample stored, under nitrogen, for several weeks showed no further change in its ^{1}H.N.M.R. spectrum.

With molar proportions of 1:2 ($[TiCl_4]:[(Me_3Si)_2O]$), the reaction proceeds more slowly and unreacted $(Me_3Si)_2O$ is still present after two days (Fig 5.8). Initially, two peaks are seen as before, but after approximately forty minutes the signal at 0.398 δppm begins to broaden and eventually splits into two singlets, viz. that at 0.412δppm due to

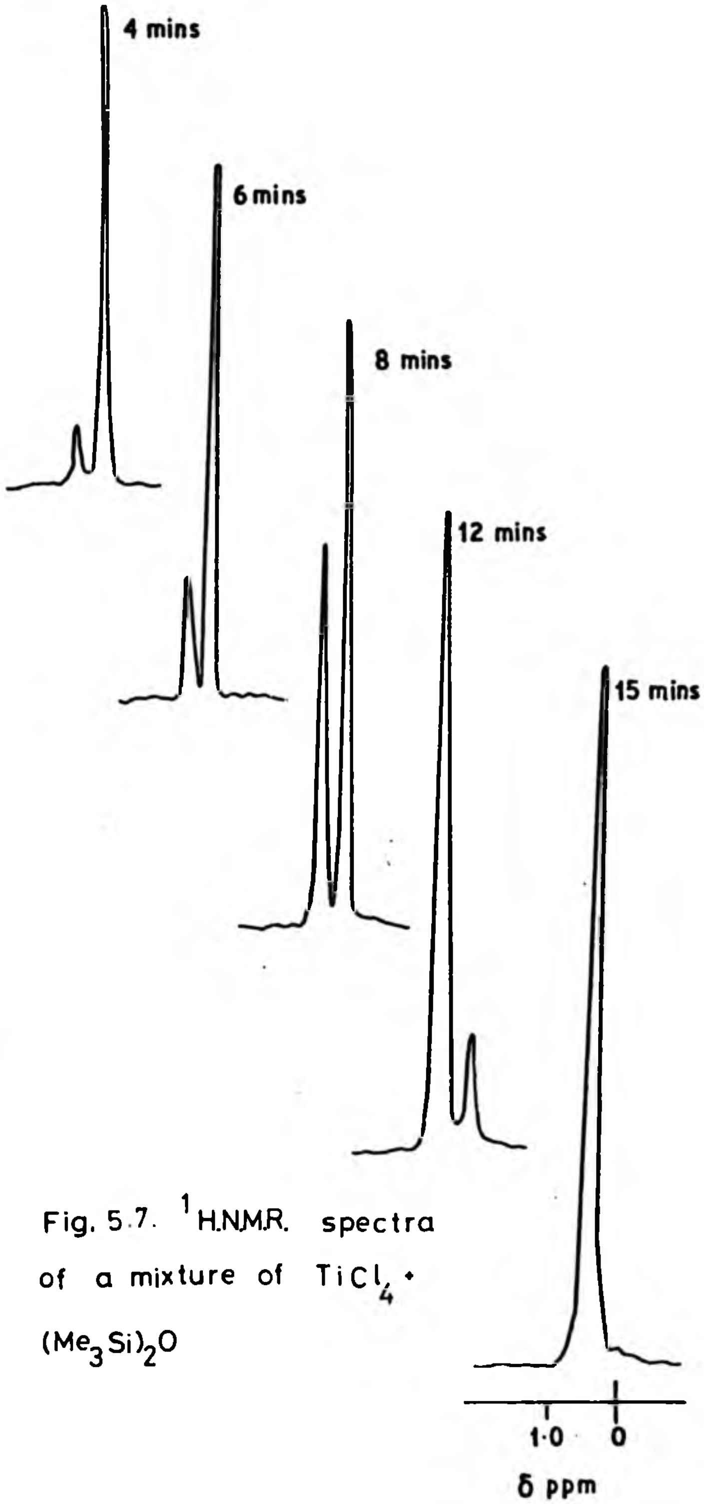


Fig. 5.7. ^{1}H.N.M.R. spectra of a mixture of $TiCl_4$ + $(Me_3Si)_2O$

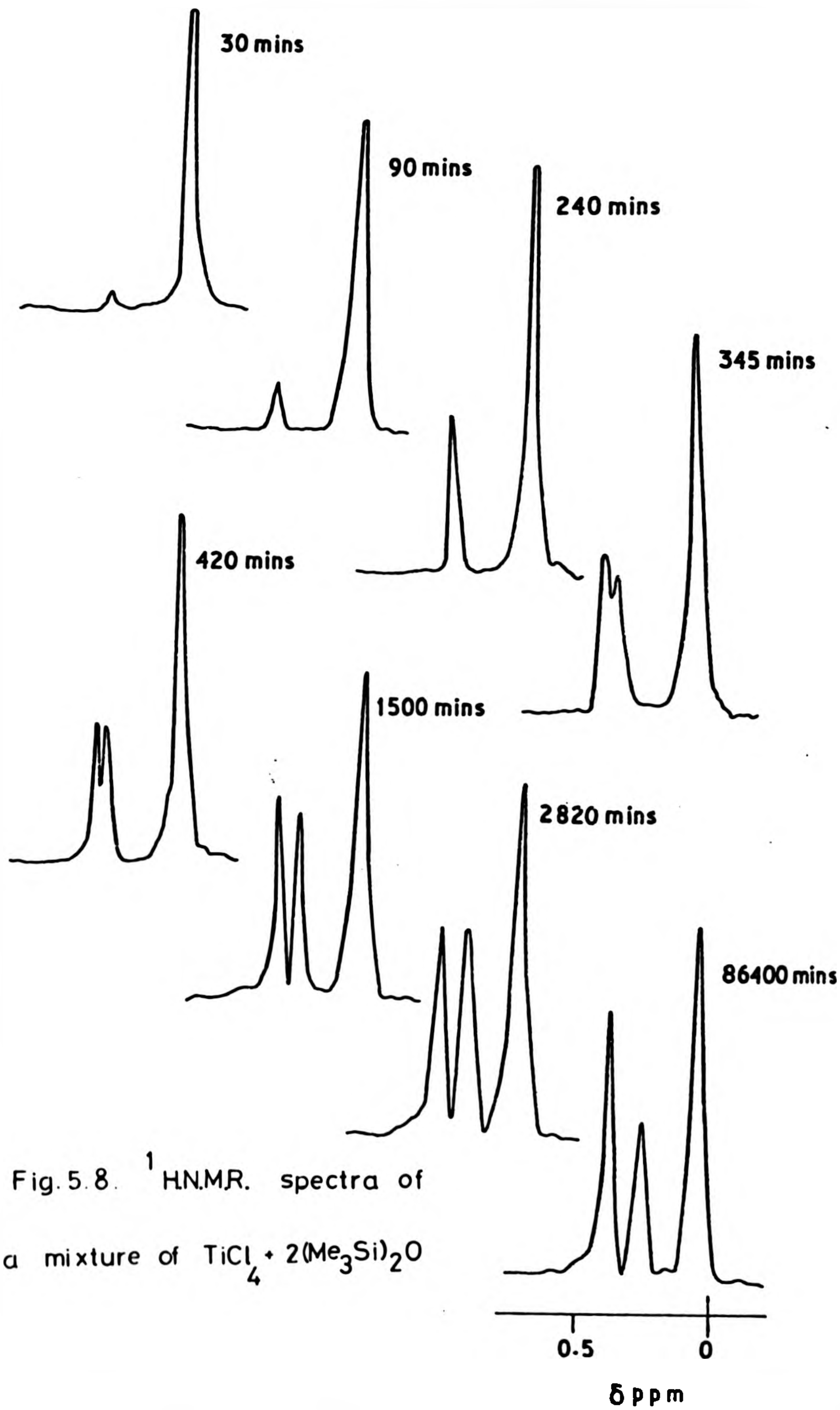


Fig. 5.8. ^{1}H.N.M.R. spectra of a mixture of $TiCl_4 + 2(Me_3Si)_2O$

Me_3SiCl and some $Me_3SiOTiCl_3$ and that at 0.326 δ ppm due to a third product, $(Me_3SiO)_2TiCl_2$:-

$$TiCl_4 + 2(Me_3Si)_2O \longrightarrow Cl_3TiOSiMe_3 + Me_3SiCl + (Me_3Si)_2O$$

$$\longrightarrow Cl_2Ti(OSiMe_3)_2 + 2Me_3SiCl$$

After another ten days a white solid slowly begins to precipitate, and ^{1}H.N.M.R. spectrum of the residual liquid shows a decrease in the intensity of the signals at 0.326 and 0.065δppm relative to that 0.412δppm. After approximately one month only two peaks at 0.412 and 0.067 δ ppm remain, indicating further reaction:-

$$Cl_2Ti(OSiMe_3)_2 \longrightarrow \frac{1}{n}[(Me_3SiO)Ti(O)Cl]_n + Me_3SiCl$$

A 1:4 mixture behaved similarly, (Fig 5.9) with precipitation of a white solid over several weeks. The residual liquid exhibited two resonances due to Me_3SiCl and unreacted $(Me_3Si)_2O$. It seems unlikely that either the tris or tetrakis (trimethylsiloxy) derivatives are formed under these conditions, since no new resonances were observed and unreacted $(Me_3Si)_2O$ remained after complete reaction.

The mono(trimethylsiloxy) derivatives, $Me_3SiOTiCl_3$, was isolated by fractionally distilling an equimolar mixture of $(Me_3Si)_2O$ and $TiCl_4$,Me_3SiCl and a colourless liquid (I), identified as $Me_3SiOTiCl_3$, were obtained. A third product was also obtained as an intractable blue-black solid in the distillation vessel, indicating thermal decomposition. The colourless liquid (I), boiling point 433-453K/760 mm Hg, exhibited one singlet at 0.370δppm in its ^{1}H.N.M.R. confirming

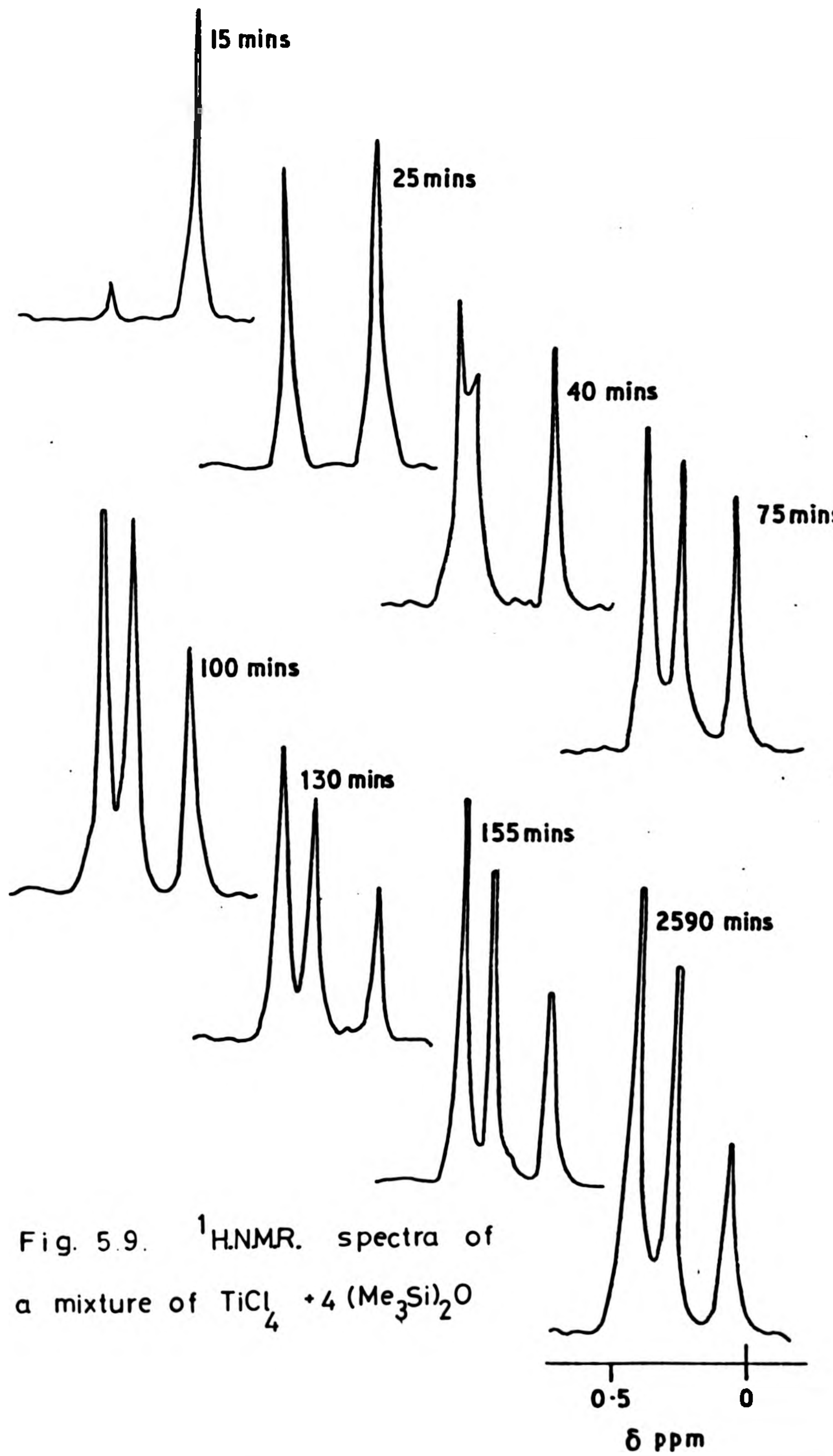


Fig. 5.9. ^{1}H.N.M.R. spectra of a mixture of $TiCl_4 + 4\,(Me_3Si)_2O$

the chemical shift observed previously in the ^{1}H.N.M.R. investigation. The infra-red spectrum (Table 5.6) is consistent with the assignment of the compound as $Me_3SiOTiCl_3$. In particular, the extremely strong band at 470cm^{-1} is characteristic of terminal (Ti-Cl) stretching mode for tetrahedral titanium species.[76,355] Complexes containing Ti-O-Si linkages have been shown to exhibit two characteristic i.r. absorptions, an intense band about 900-950 cm^{-1} and a second weaker band in the 600-500 cm^{-1} region.[326,354,356-361]

<u>Table 5.7. Silicon- Oxygen and Metal-Oxygen stretching frequencies for selected alkylsiloxymetal compounds.</u>

Compound	ν(Si-O)(cm^{-1})	ν(M-O)(cm^{-1})	Ref.
$Ti(OSiMe_3)_4$	918	517	355
$Ti(OSiMe_2Et)_4$	915	515	355
$Ti(OSiMeEt_2)_4$	915	510	355
$Ti(OSiMe_2Pr^n)_4$	917	521	355
$(C_5H_5)_2TiCl(OSiMe_3)$	939		358
$(C_5H_5)_2TiCl(OSiPh_3)$	951		358
$(C_5H_5)Ti(OSiMe_3)_3$	908		358
$[Al(OSiEt_3)_3]_2$	1064	638	355
	810	589	
		549	
$KOSiMe_3$	980		359
$(Me_3Si)_2O$	1055		342

Table 5.6 Infra-red spectral data for the products of the reaction of $TiCl_4$ with $(Me_3Si)_2O$ and related compounds (cm^{-1}).

$(Me_3SiO)Ti(O)Cl$	$(Me_3SiO)TiCl_3$	$(Me_3SiO)_4Ti$	$[(C_5H_5)Ti(O)Cl]_4$	Tentative Assignments.
			3090(m)	C-H stretch of C_5H_5
2970(m) 2930(w) 2895(w)	2950(m)	2959(s)		C-H stretch of CH_3
1450(w)	1445(w)	1451(m)		CH_3 bend
			1430(m)	C-C stretch
1410(w)	1405(w)	1401(m)		CH_3 bend
1330(vw) 1260(s) 1250(s)	1325(vw) 1255(vs) 1060(vw)	1330(w) 1248(s) 1059(m)		SiC_3 Sym. deformation

Table 5.6 continued.

$[(Me_3SiO)Ti(O)Cl]$	$[(Me_3SiO)TiCl_3]$	$[(Me_3SiO)_4Ti]$	$[(C_5H_5)Ti(O)Cl]_4$	Tentative Assignments.
			1020(s)	CH wag
985(vs) 950(m)	950(vs)	919(vs)		Si-O stretch
852(vs)	835(vs)	844(vs)		Si-C stretch, methyl rock
			800(vs)	CH wag, Ti-O-Ti stretch
755(s)	765(s)	751(s)		Si-C stretch, Methyl rock Ti-O-Ti stretcn
655(vs)	695(vw)	687(m)		Si-C stretch
635(w) 590(s)	635(s) 575(vw)	517(s)		Ti-O stretch

Table 5.6 continued.

$[(Me_3SiO)Ti(O)Cl]$	$[(Me_3SiO)TiCl_3]$	$[(Me_3SiO)_4Ti]$	$[(C_5H_5)Ti(O)Cl]_4$	Tentative Assigments.
			600(m)	ring deformation
470(vs)	475(vs)		430(s)	Ti-Cl stretch
			415(s)	Ti-C_5H_5 stretch
355(s)	370(s) 300(m)		330(s)	Ti-Cl stretch

Table 5.6 continued.

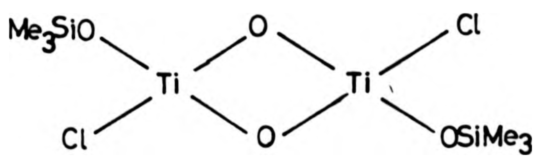
$[(Me_3SiO)Ti(O)Cl]$	$[(Me_3SiO)TiCl_3]$	$[(Me_3SiO)_4Ti]$	$[(C_5H_5)Ti(O)Cl]_4$	Tentative Assigments.
			600(m)	ring deformation
470(vs)	475(vs)		430(s)	Ti-Cl stretch
			415(s)	Ti-C_5H_5 stretch
355(s)	370(s) 300(m)		330(s)	Ti-Cl stretch

Table 5.6 continued.

$[(Me_3SiO)Ti(O)Cl]$	$[(Me_3SiO)TiCl_3]$	$[(Me_3SiO)_4Ti]$	$[(C_5H_5)Ti(O)Cl]_4$	Tentative Assigments.
			600(m)	ring deformation
470(vs)	475(vs)		430(s)	Ti-Cl stretch
			415(s)	Ti-C_5H_5 stretch
355(s)	370(s) 300(m)		330(s)	Ti-Cl stretch

Two absorptions (950(vs) and 635(s) cm^{-1}) can be located in the infra-red spectrum of (I) $(Me_3SiO)TiCl_3$, assigned to (Si-O) and (Ti-O) stretching modes respectively.

The white, air-sensitive, insoluble solid (II), precipitated on the reaction of $(Me_3Si)_2O$ and $TiCl_4$(2:1 and 4:1 molar proportions) analyses for $[(Me_3SiO)Ti(O)Cl]$. A molecular weight determination was unobtainable due to insolubility in any of the common organic solvents. An intense infra-red absorption at 470 cm^{-1} in the infra-red spectrum of the compound (Table 5.6) is attributable to a terminal ν(Ti-Cl) stretching mode for a tetrahedral titanium (IV) species.[354,355] Polymerisation via bridging chlorine seems unlikely, therefore, but the presence of bridging oxygen atoms cannot be ruled out. The two bands at 985(vs) and 950(m) cm^{-1} are tentatively assigned to (Si-O) stretching modes, and are comparable to values observed in other alkylsiloxy metal compounds.[326,354,356-361] (Table 5.7). Polymerisation via bridging oxygen atoms, whether to form heterocyclic (A,B) or chain-like(C) structures, seems highly likely.

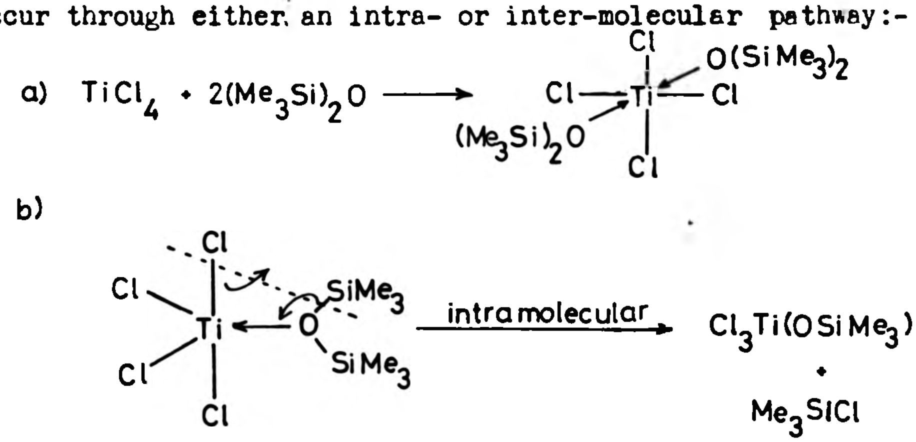


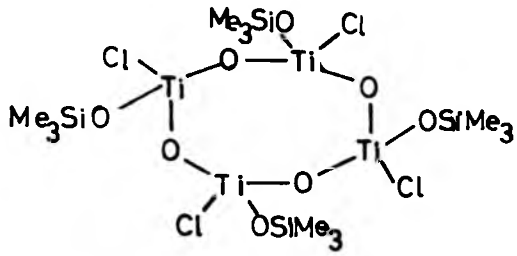
A

acceptor complexes with DMSO, DMF, THF, pyridine and dioxan failed. No reaction occured with these strong donors up to their boiling points.

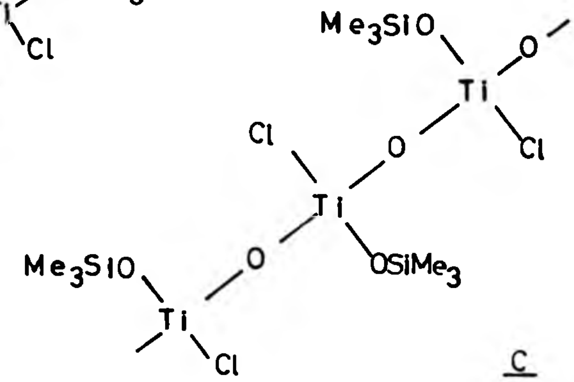
A similar complex, $[(C_5H_5)\ TiOCl]_4$, discussed in the introduction, has been shown by an x-ray structure determination to be an eight membered (Ti-O) heterocyclic system.[321,322] Without a molecular weight and/or crystal structure determination it is impossible to say whether or not our compound has a similar structure.

It is of interest to note that a yellow colouration was observed, initially, on mixing $(Me_3Si)_2O$ and $TiCl_4$, which rapidly disappears. This is interpreted as the formation of a donor-acceptor complex (step a)eg. $[TiCl_4\{(Me_3Si)_2O\}_2]$, prior to halide replacement (step b). Halide exchange may occur through either an intra- or inter-molecular pathway:-





B



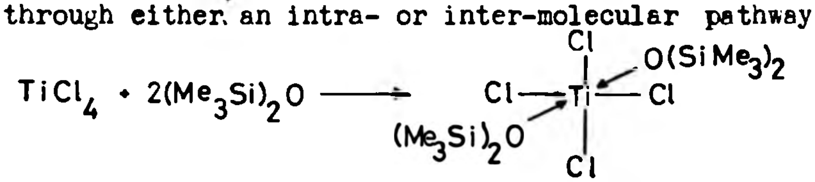
C

For the complexes $[Cl_2Ti(O)L]$ (L=MeCN, THF, $C_5H_{10}O$, $0.5C_4H_{10}O_2$ and 0.5 bipy) evidence suggests that the most likely structures are oxygen-bridged dimers or polymers. They exhibit infra-red bands in the region 790-895cm^{-1} attributed to (Ti-O) stretching modes.[362] The bis(trimethylamine) adduct, $[Cl_2TiO(NMe_3)_2]$ and its vanadium analog,[364,365] however are monomeric. This titanium complex exhibits an infra-red band assigned to ν(Ti-O) at 976cm^{-1}. It is unfortunate that for our complex, the (Si-O) stretching modes are also located in this region prohibiting unequivocal assignment of a ν(Ti-O) mode. Bridging Ti-O-Ti groups have been shown to absorb in the region 700-800cm^{-1}, for example $[(C_5H_5)TiOCl]_4$[321]: 800cm^{-1} and $[(C_5H_5)_2TiCl]_2O$[366]: 790 and 720cm^{-1}. In our complex a band is observed at 755cm^{-1} due partly to ν(Si-C) and methyl rocking modes, which may also contain a contribution from a bridging ν(Ti-O) mode. Attempts to prepare donor-acceptor complexes with DMSO, DMF, THF, pyridine and dioxan failed. No reaction occured with these strong donors up to their boiling points.

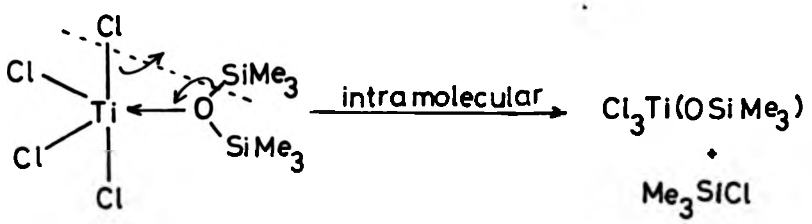
A similar complex, $[(C_5H_5)\ TiOCl]_4$, discussed in the introduction, has been shown by an x-ray structure determination to be an eight membered (Ti-O) heterocyclic system.[321,322] Without a molecular weight and/or crystal structure determination it is impossible to say whether or not our compound has a similar structure.

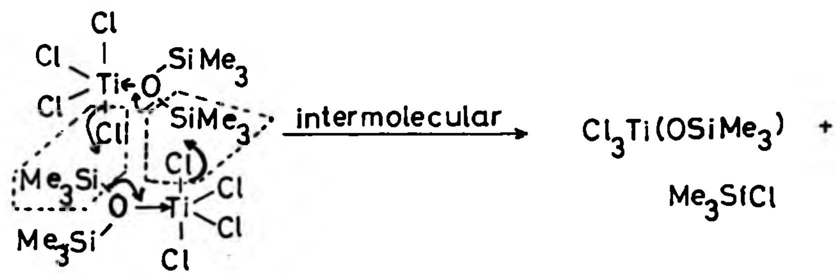
It is of interest to note that a yellow colouration was observed, initially, on mixing $(Me_3Si)_2O$ and $TiCl_4$, which rapidly disappears. This is interpreted as the formation of a donor-acceptor complex (step a)eg. $[TiCl_4\{(Me_3Si)_2O\}_2]$, prior to halide replacement (step b). Halide exchange may occur through either an intra- or inter-molecular pathway:-

a)

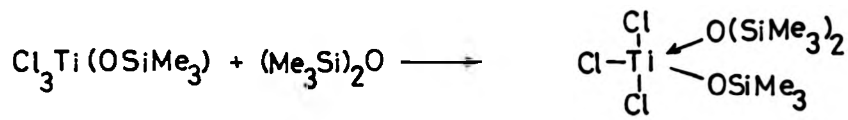


b)





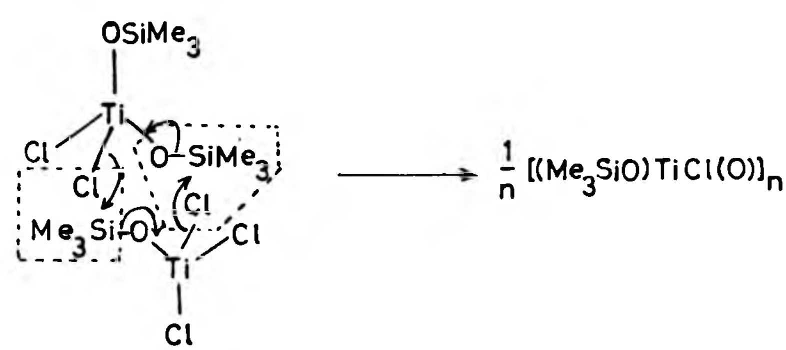
Depending on the molar ratio of $(Me_3Si)_2O$ to $TiCl_4$, more highly substituted products may be obtained (eg. steps c and d).

c) 

d) $\longrightarrow Cl_2Ti(OSiMe_3)_2 + Me_3SiCl$

The bis (trimethylsiloxy) **titanium (IV) chloride formed is** unstable with respect to further halide replacement (step e)

e)



5Aii With bis(cyclopentadienyl)titanium(IV) chloride.

No reaction occurred on prolonged heating of a mixture of $(Me_3Si)_2O$ and $(C_5H_5)_2TiCl_2$ in boiling benzene. This is in contrast to the behaviour of $TiCl_4$, presumably due to the stabilization of the Ti-Cl bonds by the presence of the electron accepting cyclopentadienyl groups. Mono-and bis-(alky or aryl-siloxy) derivatives of $(C_5H_5)_2TiCl_2$ have been prepared however by reaction with a silanol in the presence of a base or with a sodium siloxide:-[357,367.368]

$$(C_5H_5)_2TiCl_2 \quad + \quad R_3SiOH \longrightarrow (C_5H_5)_2Ti(OSiR_3)Cl + HCl$$

$$(C_5H_5)_2TiCl_2 \quad + \quad 2R_3SiONa \rightarrow (C_5H_5)_2Ti(OSiR_3)_2 + 2NaCl$$

5Aiii With zirconium (IV) chloride bis-acetonitrile.

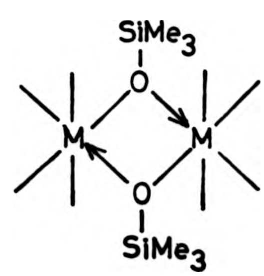
Reaction of $(Me_3Si)_2O$ with $[ZrCl_4(MeCN)_2]$, in MeCN yielded a white air-sensitive solid (III). The most likely formulation for this product is $[Cl_3Zr(OSiMe_3).MeCN]_n$, where $n > 2$, in MeCN solution. A molecular weight determination in MeCN gave a value of 828, c.f. the molecular weight for the monomer is 328, indicating some degree of association in this solvent.

The ^{1}H.N.M.R. spectrum of a $CHCl_3$ solution of the product contains two resonances in the correct intensity ratio (1.904(1) and -0.032 (3)δppm). The low-field signal is attributed to coordinated MeCN and the other to the (Me_3SiO) protons. The i.r. spectrum also confirms the presence of coordinated MeCN, in particular the ν(C=N) modes(2400(s) 2378(vs) 2340(m,sh) cm^{-1}) exhibit the expected high frequency shift.[292,369] Bands at 360(vs) and 290(vs) cm^{-1} are assigned to (Zr-Cl) stretching modes (Table 5.8).

Table 5.8 Low infra-red absorptions for [$Cl_3Zr(OSiMe_3)MeCN$] and related compounds.

Complex	Low i.r. absorptions (cm^{-1})
[$Cl_3Zr(OSiMe_3)MeCN$]	400(m,sh) 360(vs) 290(vs)
After exposure to air	400(w,sh) 360(m,sh) 315(vs)
$ZrCl_4$ [370]	405(s) 392(s) 309(m) 297(s)
$ZrCl_4(MeCN)_2$ [370]	362(s) 343(s) 314(s) 298(m)

Many trimethylsiloxy metal derivatives have high molecular weights in solution, association occuring via bridging oxygen atoms:-



$Zr(OSiMe_3)_4$ is typical in this respect.[371,372] It seems likely, therefore, that the white product (III) [$Cl_3Zr(OSiMe_3)$-MeCN], is also associated in solution as indicated by the high molecular weight value obtained. Although the molar ratio was chosen to favour the formation of a bis-substituted derivated no evidence was found for such species. Reaction of both 1:1 and 1:2 ($ZrCl_4$): $(Me_3Si)_2O$ molar proportions lead only to a mono-substituted product. $ZrCl_4$ is a polymeric solid, to aid reaction the soluble, monomeric adduct $[ZrCl_4(MeCN)_2]$ was used. Although reactivity is generally enhanced by using such monomeric adducts, it seems that in this case further reaction is not favoured. In comparison, $TiCl_4$ is very reactive being monomeric and coordinatively unsaturated, and fortuitously, reaction with $(Me_3Si)_2O$ can be carried out by simply mixing the two liquids. The reaction is fairly slow but does yield various substitution products, as previously described.

5Aiv With tin (IV) chloride.

$SnCl_4$ has been reported [373] to yield $MeSnCl_3$ and chloro derivatives of the type $RSiMe_2Cl$ (where R=Me or an extension of the siloxane chain) on reaction with $(Me_3Si)_2O$ at 543K. Methyl chloride is also abtained, arising from partial decomposition of $MeSnCl_3$. Our results confirm the formation of $MeSnCl_3$ at 323K as well. No evidence for the formation of Me_3SiCl could be found.

$$(Me_3Si)_2O + SnCl_4 \longrightarrow MeSnCl_3 + (ClMe_2SiOSiMe_3)$$

This is in complete contrast to the behaviour of $TiCl_4$, the difference has been ascribed to the higher acceptor capacity of the titanium.[373] The titanium draws away the unshared pair of electrons of the siloxane oxygen, decreasing the $(p\text{-}d)\pi$ bonding, hence weakening the Si-O bond and favouring Si-O bond fission.

5.v With chromium (III) chloride.

No reaction occured, at 323K, between $(Me_3Si)_2O$ and either $CrCl_3$ or $[CrCl_3(THF)_3]$. Formation of a donor-acceptor complex prior to halide replacement appears to be an important step in the reaction of $(Me_3Si)_2O$ with these covalent metal halides. Chromium (III) species, in general, are kinetically inert and undergo ligand substitution reactions only very slowly. Often trace quantities of reducing agents are added, to give labile Cr(II) intermediates, as catalysts for these reaction. In the case of $CrCl_3$, the Cr(II) ions can undergo electron-transfer with the inert Cr(III) ions in the solid $CrCl_3$ via chlorine bridging, enabling Cr (II) sites to be formed which can then leave the solid. If this mechanism is not possible, then the ligand must be strong enough donor to either break down the $CrCl_3$ lattice or undergo ligand exchange with a soluble complex:-

$$CrCl_{3\,(s)} + xsL \longrightarrow [CrCl_3L_3]$$

$$[CrCl_3L_3] + xsL' \longrightarrow [CrCl_3L_3'] + 3L$$

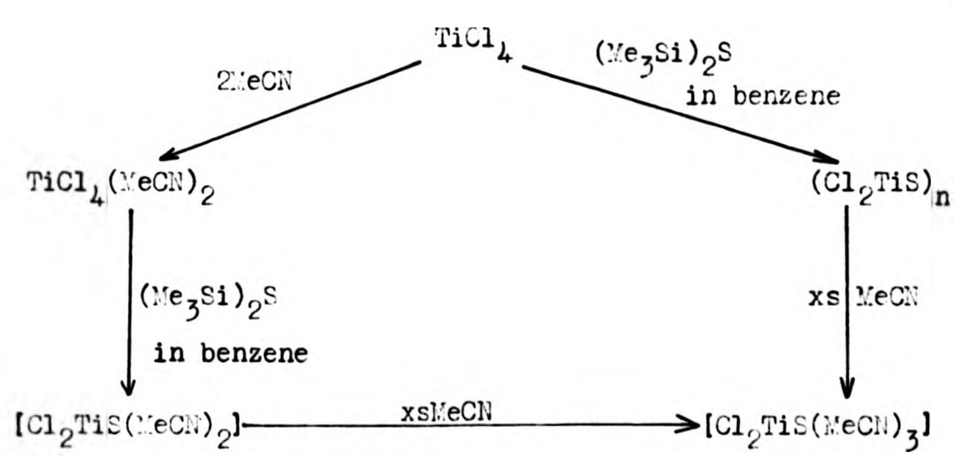
With $(Me_3Si)_2O$, the weak donor character of the oxygen atom does not facilitate the break down of the halogen bridging in the $CrCl_3$ lattice nor ligand exchange reaction with $[CrCl_3(THF)_3]$. Even if some species with coordinated $(Me_3Si)_2O$ were present, the rate of substitution is expected to be extremely slow. The lability of the Cr–Cl bond is not very high and even with $TiCl_4$, in which the Ti-Cl bond is labile, reaction with $(Me_3Si)_2O$ has been shown previously to be fairly slow.

5B Reactions of hexamethyldisilathiane:-

5Bi With Titanium (IV) Chloride.

Reaction between titanium (IV) chloride and hexamethyldisilathiane proceeds extremely rapidly, even at 96K. In a non-coordinating solvent, a dark brown solid (IV) - polymeric dichloro titanium (IV) sulphide, contaminated with a small quantity of a titanuim sulphide - is obtained. Treatment of this reaction mixture with a strong donor solvent, breaks down the polymeric lattice of $(Cl_2TiS)_n$ giving soluble monomeric adducts $[Cl_2TiS.3L]$. The titanuim sulphide impurity (V) is insoluble and is removed by filtration.

Alternatively, blocking the empty coordination sites of $TiCl_4$, for instance by using the bis-acetonitrile adduct $TiCl_4.2MeCN$, prior to reaction with $(Me_3Si)_2S$ in an inert solvent allows the bis-adduct $[Cl_2TiS. 2MeCN]$ to be isolated. The reaction is still extremely rapid and the product is easily converted to the tris-adduct with an excess of donor solvent.



Little is known about the chalcogenide halides of group IV A, only compounds with titanium having been isolated.[374] Preparation of dichlorotitanium (IV) sulphide, Cl_2TiS, using H_2S has been reported but yields are low:-[375]

$$TiCl_4 + H_2S \longrightarrow TiCl_4.H_2S \xrightarrow{273K} Cl_2TiS \xrightarrow{>409K} TiS_2$$

Very little data is available for this compound. We have shown that $(Cl_2TiS)_n$ can be prepared relatively easily from reaction of $TiCl_4$ with $(Me_3Si)_2S$. Cleavage of the Si-S bonds readily occurs, and the reaction is very rapid in a non-coordinating solvent:-

$$TiCl_4 + (Me_3Si)_2S \xrightarrow{\text{benzene}} (Cl_2TiS) + 2Me_3SiCl$$

The chemistry of titanium is dominated by its strong preference to obtain octahedral coordination and consequently (Cl_2TiS) is assumed to be polymeric via bridging halogen and/or sulphur atoms. Low infra-red absorptions at 375(s) 350(s,br) and 280(w) cm^{-1} in the solid state spectrum of this compound might well contain contributions from both (Ti-S) and (Ti-Cl) stretching modes. The likelyhood of a complex solid state structure debars formal assignment of the bands.

Adducts of dichlorotitanium (IV) sulphide were readily prepared by treatment of the solid with an excess of a donor solvent. In this way the adducts $[Cl_2TiS.3MeCN]$ and $[Cl_2TiS.3THF]$ were prepared. The bis-acetonitrile adduct was prepared by using $TiCl_4.2MeCN$ as starting material and could be converted to the tris-adduct by addition of excess acetonitrile. The infra-red spectra (Table 5.9) show the presence of coordinated solvent and low infra-red absorptions assignable to (Ti-Cl) and (Ti-S) stretching modes. In the

Little is known about the chalcogenide halides of group IV A, only compounds with titanium having been isolated.[374] Preparation of dichlorotitanium (IV) sulphide, Cl_2TiS, using H_2S has been reported but yields are low:-[375]

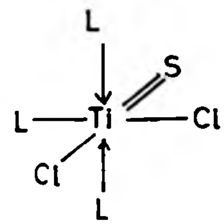
$$TiCl_4 + H_2S \longrightarrow TiCl_4.H_2S \xrightarrow{273K} Cl_2TiS \xrightarrow{>409K} TiS_2$$

Very little data is available for this compound. We have shown that $(Cl_2TiS)_n$ can be prepared relatively easily from reaction of $TiCl_4$ with $(Me_3Si)_2S$. Cleavage of the Si-S bonds readily occurs, and the reaction is very rapid in a non-coordinating solvent:-

$$TiCl_4 + (Me_3Si)_2S \xrightarrow{benzene} (Cl_2TiS) + 2Me_3SiCl$$

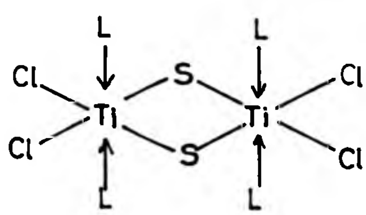
The chemistry of titanium is dominated by its strong preference to obtain octahedral coordination and consequently (Cl_2TiS) is assumed to be polymeric via bridging halogen and/or sulphur atoms. Low infra-red absorptions at 375(s) 350(s,br) and 280(w) cm^{-1} in the solid state spectrum of this compound might well contain contributions from both (Ti-S) and (Ti-Cl) stretching modes. The likelyhood of a complex solid state structure debars formal assignment of the bands.

Adducts of dichlorotitanium (IV) sulphide were readily prepared by treatment of the solid with an excess of a donor solvent. In this way the adducts [$Cl_2TiS.3MeCN$] and [$Cl_2TiS.3THF$] were prepared. The bis-acetonitrile adduct was prepared by using $TiCl_4.2MeCN$ as starting material and could be converted to the tris-adduct by addition of excess acetonitrile. The infra-red spectra (Table 5.9) show the presence of coordinated solvent and low infra-red absorptions assignable to (Ti-Cl) and (Ti-S) stretching modes. In the bis-adduct the low infra-red bands occur at slightly higher frequencies to that of the tris adduct. The tris-adducts are almost certainly monomeric, octahedral complexes(A), the positions of the low infra-red bands being characteristic of (TiCl) stretching modes for octahedral Ti(IV) species.[76]

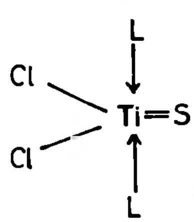


A

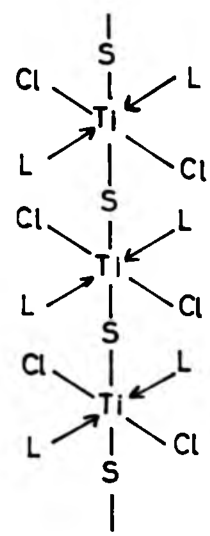
In the bis-adduct, polymerization via chlorine and/or sulphur bridges (for example B and C) is a possible alternative to a monomeric, five-coordinate structure (D).



B



D



C

Table 5.9 Selected infra-red spectral data for $(Cl_2TiS)_n$ and its MeCN and THF adducts (cm^{-1}).

$(Cl_2TiS)_n$	$[Cl_2TiS(MeCN)_2]$	$[Cl_2TiS(MeCN)_3]$	$[Cl_2TiS(THF)_3]$	Assignments
	2950(vs)	2945(w)	2950(s)	
	2920(s)	2920(w)		ν(C–H)
	2850(w)	2840(w)	2860(s)	
	2308(s)	2305(m)		ν(C≡N)
	2280(s)	2280(m)		
			1038(vs)	ν(C–O–C)
			1015(vs)	
		615(m)	665(m)	ν(Ti=S)
	400(s,sh)	400(m,sh)		
	376(s)	363(s)	365(vs)	ν(Ti–Cl)
300(vw,br)	320(m,sh)	325(vs)	325(vs)	and
		270(w)	272(w)	ν(Ti–S)
198(s,br)				

The similarity of the positions of the low infra-red bands of the bis- and tris- adducts suggests the former in the solid state. For comparison the oxygen analogues $[Cl_2TiOL_2]$, (where L = MeCN and THF) are thought to be oxygen bridged dimers or polymers, exhibit low infra-red bands at 410(sh) and 328(m) cm^{-1}. The bis (trimethylamine) adduct, in contrast, is monomeric, as shown by a crystal structure determination, and absorbs at 440(m) 410(m) 329(m) 300(sh) and 279(m-s) cm^{-1} [362,363] The (Ti-O) stretching frequencies were reported to occur at 895 and 976 cm^{-1} for the polymeric and monomeric complexes, respectively. In the case of the monomeric complex, replacement of the oxygen by sulphur would be expected to shift the ν(Ti=X) band to the 650 cm^{-1} region, assuming a similar force constant. The bands at 615(m) and 665(m) cm^{-1} for the acetonitrile and tetrahydrofuran tris-adducts, respectively, are tentatively assigned to this mode. There are no bands in similar positions in the bis-acetonitrile adduct consistent with the change from a monomeric, (Ti=S) containing complex to a sulphur bridged, polymeric species.

In an attempt to slow the reaction between $TiCl_4$ and $(Me_3Si)_2S$ even further, with a view to discrete ring formation, $(Me_3Si)_2S$ was added dropwise into an acetonitrile solution of $TiCl_4.2MeCN$. No obvious immediate reaction was observed but a very fine precipitate was formed on refluxing for several hours. The precipitate could not be filtered from the solution as it was too fine, removal of solvent by vacuum distillation gave a yellow solid (IA). This product was shown to contain coordinated MeCN by infra-red and ^{1}H.N.M.R. spectroscopy. Its mass spectrum contained lines of higher m/e values than that for the molecular ions of both $TiCl_4.(MeCN)_2$ and $[Cl_2TiS.(MeCN)_3]$. The highest m/e values observed appeared at ~460, which might correspond to $[\{Cl_2TiS.(MeCN)_2\}_2]^+$ (m/e = 464) but no fragmentation pattern corresponding to this complex could be determined. Without further purification to ensure removal of unreacted $TiCl_4.2MeCN$ and any other side products further characterization of the yellow solid could not be attempted. Unfortunately the product exhibited the same solubility as the parent compound and attempted separation by column chromatography only lead to hydrolysis.

It would seem that ring formation in this system is unfavourable. Choice of conditions to favour ring formation, eg. dilute solutions, slowing reaction rates via blocking of the coordination sites of the metal and by use of low temperatures, only gave highly polymeric or monomeric species. The product $(Cl_2TiS)_n$ being of the former type, giving novel adducts, $[Cl_2TiS.3L]$, of the latter type with strong donors (eg. L=THF or MeCN).

5Bii With bis (cyclopentadienyl) titanium (IV) chloride.

No reaction was observed between $(C_5H_5)TiCl_2$ and $(Me_3Si)_2S$ at 353K. This is surprising since the Si-S bonds of Me_3SiSR type compounds undergo fission with various transition-metal halides including $(C_5H_5)_2TiCl_2$.[344]

$$(C_5H_5)TiCl_2 + 2Me_3SiSPh \longrightarrow (C_5H_5)_2Ti(SPh)_2 + 2Me_3SiCl$$

$$2NiCl_2 + 2Me_3SiSMe \longrightarrow \frac{1}{6}[Ni(SMe)_2]_6 + \frac{1}{n}[Ni(SMe)_2]_n + 2Me_3SiCl$$

5Biii With zirconium (IV) chloride bis (acetonitrile).

Addition of $(Me_3Si)_2S$ to a MeCN solution of $[ZrCl_4(MeCN)_2]$ lead to the formation of a bright orange solid (X) which has not been fully characterized. Analytical data was inconclusive, although a low chloride analysis suggests that halide replacement occurs. Infra-red and ^{1}H.N.M.R. spectral data indicate coordinated MeCN, exhibiting absorptions at 2305(s) and 2280(vs) cm^{-1} in its i.r. spectrum and a resonance at 1.89 ppm in its proton N.M.R. spectrum. The ^{1}H.N.M.R. spectrum also contains a second resonance (-0.046ppm), in the region expected for Me_nSi - groups, possibly due to linkages of the type $(Me_3Si-S-Zr)$ This work is incomplete as it is being further studied in this laboratory. Since we have shown that $(Me_3Si)_2S$ provides a useful route to the complexes $Cl_2TiS.L_3$ (L=MeCN or T.H.F.), further work is being carried out with the view of preparing other novel halogenosulphides, eg by reaction with WCl_4, $MOCl_4$, VCl_4 etc. Further analogous halogenoselenides may be possible by using $(Me_3Si)_2Se$.

5Biv With tin (IV) chloride.

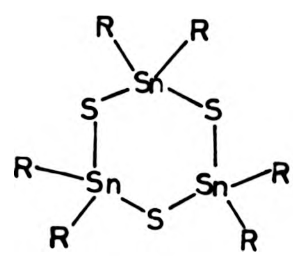
There are numerous examples of group IVB containing heterocycles.[107] Although there are very few confirmed examples of tin-oxygen heterocycles, there are many rings containing alternative tin and sulphur atoms. The majority of these (Sn-S) rings are organic derivatives of six-membered rings (E), which are easily prepared from the dialkyl tin (IV) halides with H_2S, Na_2S or $(NH_4)_2S$.[376,378]

$$Et_2SnCl_2 + Na_2S \longrightarrow \frac{1}{3}(Et_2SnS)_3 + 2NaCl$$

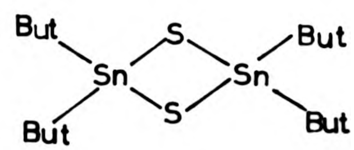
Reaction with CS_2 has also been used.[379]

$$Ph_2SnCl_2 + CS_2 \longrightarrow \frac{1}{3}(Ph_2SnS)_3 + CSCl_2$$

A dimer, $(Bu^t_2SnS)_2$, has recently been synthesised, and shown by an x-ray structural analysis to contain a flat four-membered (Sn-S) ring[337] (F).

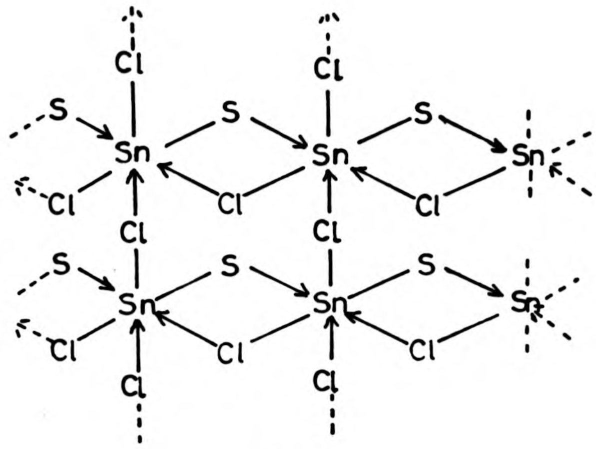


E



F

It was hoped that reaction of $SnCl_4$ and $(Me_3Si)_2S$ would give heterocyclic products, however the mustard coloured product (XI) obtained is almost certainly polymeric. The reaction proceeded rapidly in benzene solution, giving the product as yellowy-brown precipitate, which analysed for (Cl_2SnS). Insolubility in common organic solvents procluded a molecular weight determination. Unlike its titanium analogue, treatment with a variety of donor solvents did not give soluble monomeric adducts. The low infra-red absorptions at 325 and 260 cm^{-1} are attributed to Sn-Cl and Sn-S stretching modes Both halogen and sulphur bridging seems likely, eg as in (G).



G

For comparison, bridging, ν(Sn-S-Sn), modes have been located at 365 and 320 cm^{-1} in other (Sn-S-Sn) containing compounds.[380]

5Bv With dimethyl tin(IV) chloride.

Confirmation that $(Me_3Si)_2S$ could be used to prepare heterocyclic componds was provided by the formation of the cyclic trimer $(Me_2SnS)_3$ on reaction of Me_2SnCl_2 with $(Me_3Si)_2S$:-

$$Me_2SnCl_2 \ + \ (Me_3Si)_2S \rightarrow \tfrac{1}{3}(Me_2SnS)_3 \ + \ 2Me_3SiCl$$

The reaction proceeds more slowly than the analogous $SnCl_4$ and $TiCl_4$ reactions.

5Bvi With titanium (III) chloride tris (tetrahydrofuran.)

$(Me_3Si)_2S$ reacts with $[TiCl_3(THF)_3]$ in THF solution, giving a charcoal grey precipitate (XII). Purification of the product was hampered by its extreme air/moisture sensitivity. However infra-red evidence confirms the presence of coordinated THF, with the characteristic absorptions at 1035 and 1005 cm^{-1} due to ν_{as} (C-O-C). Low energy bands at 355(vs) 325(vs) 295(s,br) and 270(s,br) cm^{-1} are assigned to ν(Ti-Cl) and ν(Ti-S) modes. Analytical data was not conclusive but a formulation

[ClTiS(THF)$_{1.5}$] is suggested and a polymeric structure likely.

5Bvii With vanadium (III) chloride tris(tetrahydrofuran).

Treatment of a THF solution of [$VCl_3(THF)_3$] with $(Me_3Si)_2S$ resulted in the surprising formation of a black insoluble vanadium sulphide (XIII). No coordinated solvent was present. Analytical data suggests the formulation [$ClVS_4$], however this limited data must be treated with caution. The chloride analysis was variable, probably due to interference by the sulphide. Structures based on sulphur and/or chloride bridges to give polmeric networks are envisaged.

5Bviii With chromium (III) chloride tris(tetrahydrofuran)

A brown solid (XIV), which analyses for [ClCrS(THF)$_{1.5}$], was obtained on reaction of THF solutions of [$CrCl_3(THF)_3$] and $(Me_3Si)_2S$. Coordinated THF was confirmed by i.r. spectral data, in particular the characteristic ν_{as}(C-O-C) bands (1035 and 1015 cm^{-1}). Additional evidence was furnished by its proton N.M.R. spectrum, which exhibited resonances, of equal intensity, at 3.595 and 1.759δppm. Low i.r. absorptions at 365(s,sh) 340(vs,br) 310(m) and 285(w) cm^{-1} are attributed to terminal and bridging (Cr-Cl) and (Cr-S) stretching vibrations. As with its Ti(III) analogue a complex polymeric structure seems likely.

CHAPTER SIX.

REACTIONS OF BIS(CYCLOPENTADIENYL) BIS(ETHANETHIOLATO)-TITANIUM (IV) WITH COVALENT TRANSITION METAL HALIDES -ATTEMPTED PREPARATION OF MIXED-VALENCE COMPOUNDS.

INTRODUCTION.

Mixed-valence systems are of interest because their properties are rarely just the sum of the properties of the different metal ions. For example many show unusually intense colourations, the best known of which is probably deep blue $KFe^{III}Fe^{II}(CN)_6$ formed by reaction of pale yellow $K_4Fe^{II}(CN)_6$ and $Fe_2^{III}(SO_4)_3$. Other maybe electrical conductors, eg $Li_xW_x^{V}W_{(1-x)}^{VI}O_3$, whereas their constituent ions are insulators.

Robin and Day[381] proposed a classification of these compounds, according to the more or less delocalized character of their valence electrons:-

Class I includes those compounds in which valences are so firmly trapped that no interaction occurs and their properties are just the sum of the properties of their components.

Class II contains complexes where there is only a slight delocalization in the ground state, and, as a first approximation, different integral oxidation states can be ascribed to the constituent elements. However a valence exchange can occur through two mechanisms:-

a) by light absorption, generally in the visible part of the spectrum, termed intervalence transfer absorption.

b) by thermal exchange which constitutes an internal homonuclear redox reaction, ie hopping.

Class III in the other limiting case, compounds exhibit a complete delocalization of valence electrons via polycentric molecular orbitals and no integer oxidation states can be ascribed to the constituent metal ions.

INTRODUCTION.

Mixed-valence systems are of interest because their properties are rarely just the sum of the properties of the different metal ions. For example many show unusually intense colourations, the best known of which is probably deep blue $KFe^{III}Fe^{II}(CN)_6$ formed by reaction of pale yellow $K_4Fe^{II}(CN)_6$ and $Fe_2^{III}(SO_4)_3$. Other maybe electrical conductors, eg $Li_xW^{V}_{x}W^{VI}_{(1-x)}O_3$, whereas their constituent ions are insulators.

Robin and Day[381] proposed a classification of these compounds, according to the more or less delocalized character of their valence electrons:-

Class I includes those compounds in which valences are so firmly trapped that no interaction occurs and their properties are just the sum of the properties of their components.

Class II contains complexes where there is only a slight delocalization in the ground state, and, as a first approximation, different integral oxidation states can be ascribed to the constituent elements. However a valence exchange can occur through two mechanisms:-

a) by light absorption, generally in the visible part of the spectrum, termed intervalence transfer absorption.

b) by thermal exchange which constitutes an internal homonuclear redox reaction, ie hopping.

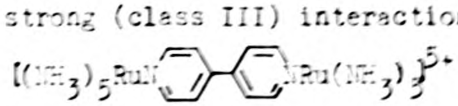
Class III in the other limiting case, compounds exhibit a complete delocalization of valence electrons via polycentric molecular orbitals and no integer oxidation states can be ascribed to the constituent metal ions.

It therefore follows that the extent to which an electron can be regarded as being localized at a particular donor site in the ground state is of fundamental importance when considering these systems. The extent of delocalization is dependent on two factors:-

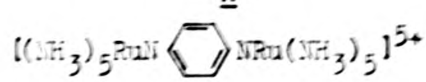
a) direct overlap of the orbitals of the two metal atoms.

b) metal-ligand-metal overlap, characteristically through σ- or π-metal-ligand bonding.

Since the reviews of Allen and Hush,[382,383] and Robin and Day,[381] much interest has been shown in mixed-valence compounds and many examples representing diverse structural types have been studied.[384,392] The change from class II to class III compounds is obviously not distinct, and the series A to C exemplify the three possibilities of weak (class II), moderate and strong (class III) interaction.[389,390]



A



B

$[(NH_3)_5RuN{\equiv}C{-}C{\equiv}NRu(NH_3)_5]^{5+}$

C

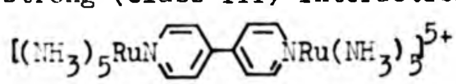
In complex A there is very little interaction between the ruthenium atoms. The complex exhibits a low energy absorption, which is subject to strong solvent shifts and has the predicted half-width expected for a long range charge transfer process. Complex B exhibits a similar low-energy band which is relatively narrow and not appreciably solvent dependent.

It therefore follows that the extent to which an electron can be regarded as being localized at a particular donor site in the ground state is of fundamental importance when considering these systems. The extent of delocalization is dependent on two factors:-

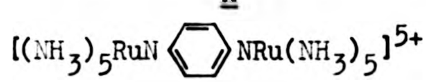
a) direct overlap of the orbitals of the two metal atoms.

b) metal-ligand-metal overlap, characteristically through σ- or π-metal-ligand bonding.

Since the reviews of Allen and Hush,[382,383] and Robin and Day,[381] much interest has been shown in mixed-valence compounds and many examples representing diverse structural types have been studied.[384,392] The change from class II to class III compounds is obviously not distinct, and the series A to C exemplify the three possibilities of weak (class II), moderate and strong (class III) interaction.[389,390]



A



B

$$[(NH_3)_5RuN{\equiv}C{-}C{\equiv}NRu(NH_3)_5]^{5+}$$

C

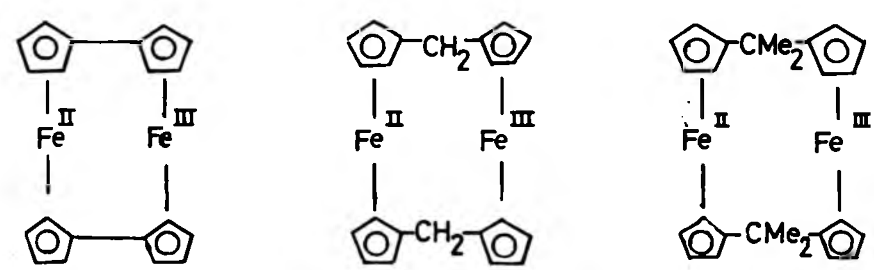
In complex A there is very little interaction between the ruthenium atoms. The complex exhibits a low energy absorption, which is subject to strong solvent shifts and has the predicted half-width expected for a long range charge transfer process. Complex B exhibits a similar low-energy band which is relatively narrow and not appreciably solvent depenendent.

There is evidence of appreciable delocalization in the ground state, and although the exact nature of this complex is subject to controversy, there is little doubt that the valencies are subject to a rapid thermal exchange reaction:-

$$[Ru(II)\text{-}Ru(III)]^{5+} \rightleftharpoons [Ru(III) - Ru(II)]^{5+}$$

Complex C is of the average valency type.[390] Again there is a near i.r. electronic absorption but it is narrower than expected for an intervalence band and it is not subject to solvent shifts.

The difficulties of interpretation in some of these systems are well illustrated by the sequence of ferrocene derivatives D to F :[384,385,390]



D E F

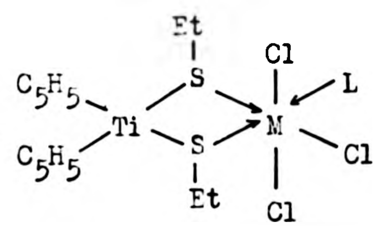
The spectrum of D shows a near i.r. band as expected for a mixed-valence complex. This absorption has a shoulder and at low temperature is resolved into two bands. Complex E has a well defined band ascribed to intervalence transfer but with F no such band is observed.

In general, if the ions in a mixed-valence complex are in exactly equivalent sites the complex will be of class III.

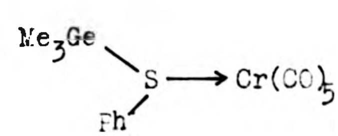
However, although the tungsten atoms in $[W_4O_8Cl_8(H_2O)_4]^{2-}$ are crystallographically equivalent, the complex has been shown by E.S.CA. and E.S.R. studies[388] to contain two W(V) and two W(VI) ions. The complex is considered to be of class II and the electronic spectrum contains two intense bands assigned to intervalence W(V) - W(VI) transitions.

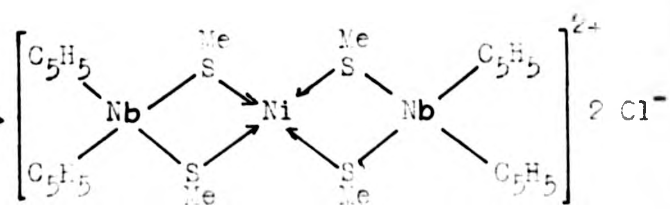
One of the distinguishing features of the early transition metal is their ability to exhibit various oxidation states within a wide range of compounds. Yet mixed-valence systems of the elements have been little studied. It has been shown that solutions of Ti(III,IV) in concentrated sulphuric acid are black, the most intense absorption corresponding to a Ti(III)/Ti(IV) ratio of 1:1.[393] Similarly partial oxidation of skyblue Ti(III) solutions in 12MHCl gives a deep purple colouration.[394] The spectra of these solutions were said to be a superposition of the d-d bands and an intense new band, the species responsible for the latter, however, have not been identified. In an investigation concerning the preparation and spectral properties of complex cyanides of vanadium, a deep blue compound, formula $[K_7V_2(CN)_{11}(OH)]$, was obtained.[395] Oxidation state titrations gave a value of ~2.7 for the oxidation state of the vanadium. This was seen to indicate the presence of both V(II) and vanadium in some higher oxidation state. The product was not completely characterized but was thought to be a class II complex. Chromium may assume a wide variety of valences and consequently the possible combinations of mixed-valence systems is large. However very little work has been carried out in this area. Mixing Cr(III) and $Cr^{VI}O_4^{\ 2-}$ in acidic solution leads to the formation of a 1:1 complex ion $[Cr^{III}\ Cr^{VI}O_4]^+$. The stoichiometry of this complex was determined using its interaction absorption band at $14{,}300 cm^{-1}$, a class II system is thus inferred.[396]

This ability to exhibit various oxidation states was just the situation we wished to exploit in studying the possible synthesis of homo- and hetereo- nuclear mixed-valence species of the early transition metals. We hoped to use bis(thiolato) metal complexes as ligands to other appropriate metal ions.

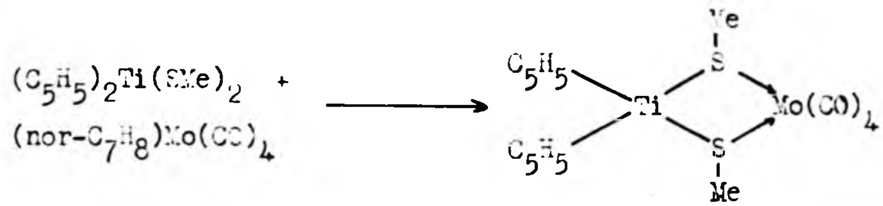
eg. $(C_5H_5)_2Ti(SEt)_2 + MCl_3L_3 \longrightarrow$ 

A feature of many thiolato-sulphur atoms is their tendency to form bridges to adjacent metal ions. The use of thiolato metal complexes as ligands has been well illustrated:-[397-411]

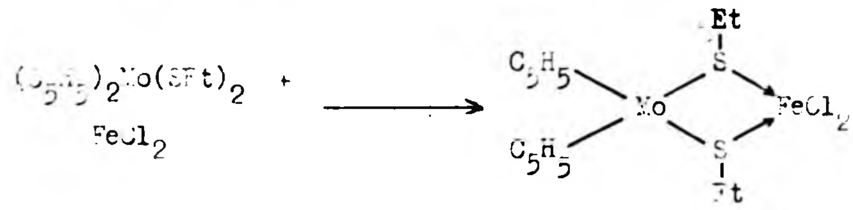
a) $Me_3GeSPh + Cr(CO)_6 \longrightarrow$ 

b) $(C_5H_5)_2Nb(SMe)_2 + NiCl_2 \longrightarrow$ 

c)



d)



In these binuclear complexes an interaction between the metal atoms may occur. Consider the series $[(C_5H_5)_2M(SR)_2M'(CO)_4]$ (M=Ti, R=Me, Ph, M'=Mo; M=W, R=Ph, M'=Cr, Mo, W). The Ti(IV) complex exhibits an intense low-energy charge transfer band, overlapping but distinguishable from the lowest energy absorption in $(C_5H_5)_2Ti(SMe)_2$, indicating considerable M-M' bonding.[402] A crystallographic study of the complex shows a planar (TiSMoS) ring in which the SMoS and STiS angles are obtuse, supporting evidence for significant Ti-Mo interaction[412] (Fig 6.1). In contrast the tungsten (IV) complexes (Table 6.1 and 6.2) show

Table 6.1 Molecular dimensions for the complexes $[(C_5H_5)_2M(SR)_2M'(CO)_4]$

	W-W	W-Mo	W-Cr	Ti-Mo
M-M'	4.01	4.06	3.93	3.32
M'-S	2.48	2.50	2.49	2.46
M-S	2.58	2.62	2.49	2.56
$\widehat{SM'S}$	72.8°	72.6°	72.1°	99.9°
$\widehat{SMS}$	69.4°	69.0°	72.0°	94.6°
$\widehat{MSM'}$	104.9°	105.0°	104.2°	8[illegible].8°

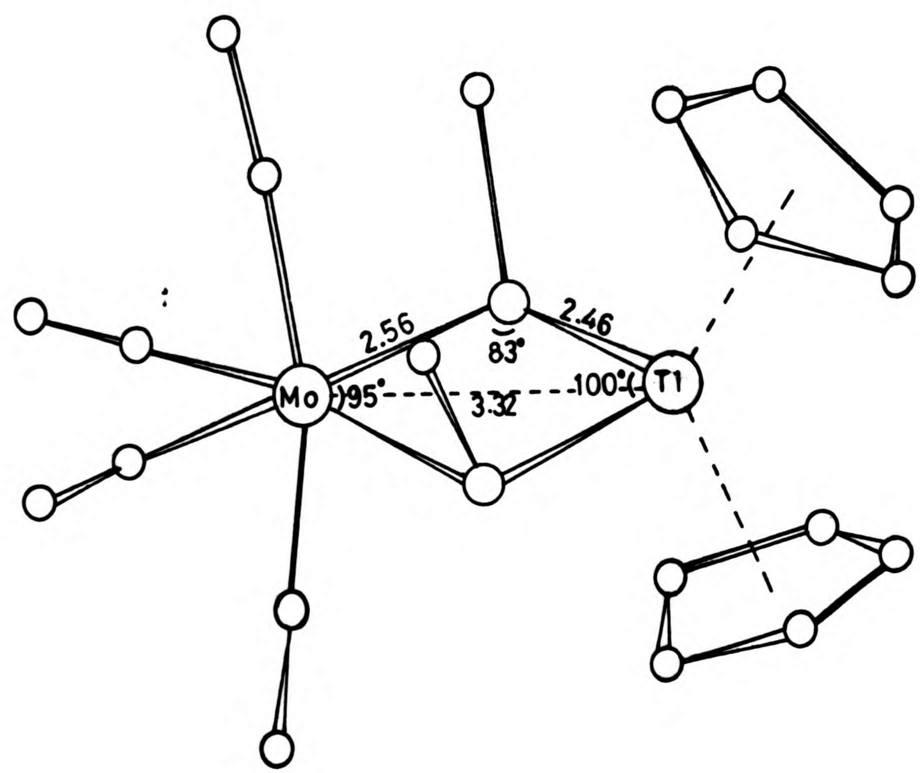


Fig. 6.1. Molecular Structure of $[(h^5C_5H_5)_2\,Ti(SMe)_2\,Mo(CO)_4]$.

no evidence for any metal-metal bonding.[403]

Table 6.2 Selected spectral data for the complexes $[(C_5H_5)_2M(SR)_2M'(CO)_4]$ and related compounds (cm^{-1})

Complex	ν(C-O)	Electronic transitions
$[(C_5H_5)_2W(SPh)_2Mo(CO)_4]$	2010, 1898, 1870 1850, 1842, 1817	
$[(C_5H_5)_2Ti(SPh)_2Mo(CO)_4]$	2018, 1930, 1912 1899,	18600, 16000
$[(PhSC_2H_4SPh)Mo(CO)_4]$	2027, 1905, 1868	None
$[(C_5H_5)_2Ti(SPh)_2]$	-	18600

We have studied the reactions of $(C_5H_5)_2Ti(SEt)_2$ with the tervalent metal halides of titanium, vanadium and chromium in a preliminary investigation into the synthesis of mixed-valence compounds. From the limited evidence so far collected for this series it seems that ligand exchange occurs rather than the formation of the desired mixed-valence species.

EXPERIMENTAL

Reactions of bis(cyclopentadienyl) bis (ethanethiolato)-titanium (IV):

6i With titanium (III) chloride tris (tetrahydrofuran).

$TiCl_3(THF)_3$ (0.74g;2.00mmols) and $(C_5H_5)Ti(SEt)_2$(0.66g;2.20mmols were placed in an ampoule, then THF(75cm^3) distilled on under reduced pressure. The ampoule was sealed under vacuum. The purple solution slowly turned red over a period of several days. Removal of solvent yielded a red solid from which $(C_5H_5)_2TiCl_2$ could be obtained by recrystallization from $CHCl_3/CCl_4$ or by column chromatography with carboxymethylcellulose / benzene. A second grey fraction was observed on the chromatography column but could not be isolated.

6ii With vanadium (III) chloride tris (tetrahydrofuran).

VCl_3(1.54g;9.83mmols) was extracted with THF (150cm^3)via a soxhlet thimble, the brick red solution obtained was added to $(C_5H_5)_2Ti(SEt)_2$(3.01g;10.00mmols) in an ampoule. The ampoule was evacuated and sealed at 96K. A brown-red solution developed from which a red-brown solid was obtained on removal of solvent. Extraction of this solid with either toluene or Et_2O gave $(C_5H_5)_2TiCl_2$(1.9g;76%) and a brown insoluble residue (I).

Brown solid (I).

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 3400 - 3100(s,br) 2955(s) 2920(s) 2860(m) 1600(m) 1485(m) 1445(m) 1365(m) 1260(m) 1080(w) 1040(w,sh) 1010(s) 910(w) 850(s) 810(s) 720(s) 660(s,br) 530(s,br)

Chemical Analysis (%) Found, C:20.85, H:3.38, Cl:10.48

6iii With chromium (III) chloride tris (tetrahydrofuran).

a) $CrCl_3$(2.65g;16.75mmols) was extracted with THF (150cm^3) via a soxhlet thimble, and the mauve solution added to $(C_5H_5)_2Ti(SEt)_2$(5.00g;16.65mmols) in an ampoule. The ampoule was evacuated and sealed at 96K. A red-brown solution and a green solid developed within 24 hours. The olive-green solid (II) was collected by filtration and thoroughly washed with THF and n-hexane. The filtrate was evaporated to dryness and recrystallised from $CHCl_3/CCl_4$ to give $(C_5H_5)_2TiCl_2$(3.6g;87%).

Green solid (II)

Infra-red Data (cm^{-1},nujol and H.C.B.mulls) 2972(m,sh) 2955(m) 2920(s) 2860(m) 1445(m) 1425(m) 1370(m) 1252(vs) 1235(w,sh) 1048(w) 1025(w) 965(m) 860(vs) 815(vw) 760(m) 720(m) 675(vw) 655(w) 392(s) 338(s) 330(vs,sh) 320(s,sh) 305(s) 280(m)

Chemical Analysis (%) Found; C:24.95, H:4.74, Cl: 10.70, S:35.41, Calc'd for $C_8H_{16}ClCrO_2S_4$, C:26.70, H:4.49, Cl:9.85, S:35.63.

b) A mauve solution of $CrCl_3(THF)_3$, obtained by extraction of $CrCl_3$(0.44g;2.78mmols) with refluxing THF (150cm^3), was added to $(C_5H_5)_2Ti(SEt)_2$(0.53g;1.77mmols) in an ampoule. The ampoule was evacuated and sealed at 96K. Over several months the solution changed colour from purple to red-brown to green to turquoise to finally, blue. The blue solution was concentrated then n-hexane added to precipitate a dark blue solid(II).

Blue solid (III)

Infra-red Data (cm^{-1};THF and $CHCl_3$ solutions) 2980(m) 2950(s)

2925(s) 2860(m) 1500(w) 1465(w) 1440(w) 1410(w) 1350(vw) 1320(vw) 1255(w) 1235(w) 1135(w) 1110(m) 1085(s) 1055(vs) 1020(vs) 970(w) 880(vw,br) 815(s) 755(m) 720(m) 670(m) 565(m) 535(m) 505(m) 390(vs) 340(w) 310(w) 285(w) 275(w)

^{1}H.N.M.R. Data (ppm; ref TMS; C_6D_6 solution) 1.460(1) broad, 3.618(1) broad.

Electronic spectrum (cm^{-1}; THF solution) 15152, 19152,

Chemical Analysis (%) Found C:31.49, H:4.59, Cl:1086, S:2.91. MWt:346

6iv With titanium (IV) chloride.

A benzene solution of $(C_5H_5)_2Ti(SEt)_2$(0.33g;1.10mmols) was placed in an ampoule, and $TiCl_4$(0.1cm^3,0.91mmols) added via a syringe. The ampoule was degassed and sealed at 96K. Immediate reaction occurred giving a dark red solution, removal of solvent yielded a red solid which was recrystallized from $CHCl_3/CCl_4$ and shown to be $(C_5H_5)_2TiCl_2$(0.23g;84%). Fractional distillation of the solvent yielded a trace of a malodorous liquid identified as diethyl sulphide.

6v. With titanium (IV) chloride bis (acetonitrile).

A solution of $TiCl_4$ (0.7cm^3;6.37mmols) in MeCN (75cm^3) was added to $(C_5H_5)_2Ti(SEt)_2$ (1.9g;6.35mmols) in an ampoule which was then sealed. A red solid and solution formed, which on removal of solvent yielded an inhomogeneous red and yellow-brown solid. Extraction of the solid with $CHCl_3$ gave $(C_5H_5)_2TiCl_2$ and a brown residue (IV).

Brown solid (IV).

Infra-red Data (cm^{-1}; nujol and H.C.B.mulls) 3300(m,br)

3090(s) 2960(m) 2920(m) 2305(m) 2280(s) 1640(w) 1480(w) 1435(s) 1410(m) 1360(m) 1260(m) 1215(w) 1015(m) 860(s,br) 730(vs,br) 450(m) 390(vs) 315(m)

Chemical Analysis (%) Found, C:21.72, H:2.75 N:4.89, Cl:31.58 S:7.28.

6vi With dimethyl tin (IV) chloride.

$(C_5H_5)_2Ti(SEt)_2$(1.58g;5.25mmols), Me_2SnCl_2(1.35g;6.13mmols and benzene (75cm^3) were placed in an ampoule, which was then degassed and sealed. A red solution rapidly developed from which $(C_5H_5)_2TiCl_2$ was recovered (1.3g;82%) The volatile fraction was fractionally distilled to give a small quantity of a malodorous liquid identified as diethyl sulphide.

6vii With diiron enneacarbonyl.

$Fe_2(CO)_9$(0.79g;2.17mmols) and $(C_5H_5)_2Ti(SEt)_2$(0.65g;2.16 mmols) were replaced in an ampoule, THF was then distilled on under vacuum, and the ampoule sealed. The purple solution slowly turned dark red and yielded a brown-red solid on removal of solvent. Sublimation of a portion of the product at 323-333K/0.01mm Hg, gave an orange solid identified as $[Fe_2(CO)_6(SEt)_2]$ and a brown residue (V). A second portion was thoroughly washed with n-hexane, to remove $[Fe_2(CO)_6(SEt)_2]$ leaving a brown solid (VI).

Brown solid (V).

Infra-red Data (cm^{-1}; nujol and H.C.B.mulls) 3090(w) 2960(vs) 2920(vs) 2850(s) 2070(s) 2030(vs) 1985(vs) 1945(s,sh) 1900(m,sh) 1450(m) 1375(m) 1260(s) 1095(s) 1015(s)

860(m) 795(s) 720(m) 618(m) 575(m) 565(m) 390(w) 370(w)

^{1}H.N.M.R. Data (δppm; ref TMS; $CDCl_3$ solution) 6.34(5,broad) 6.29(5,broad) 2.65(4,broad) region 2-0 δppm obscured by grease impurity.

Brown solid (VI)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 3100(m) 2960(m) 2925(m) 2860(w) 2070(vs) 2035(vs) 1998(vs) 1985(vs) 1940(m,sh) 1910(v,sh) 1780(m) 1440(m) 1375(w) 1360(w) 1255(w) 1090(m) 1065(m) 1015(s) 855(m,sh) 800(s,br) 740(w) 720(w) 615(w) 575(m) 555(m) 490(m) 425(m) 415(m) 395(m) 350(w)

^{1}H.N.M.R. Data (δppm;ref TMS;$CDCl_3$solution) 6.55

DISCUSSION

Reactions of bis(cyclopentadienyl) bis(ethanethiolato)titanium(IV)

As a general rule reaction of $(C_5H_5)_2Ti(SEt)_2$ with the tervalent metal halides, MX_3(M=Ti,V,Cr,X=Cl), yielded $(C_5H_5)_2TiCl_2$ and a second, unidentified, product.

$$(C_5H_5)_2Ti(SEt)_2 + MCl_3(THF)_3 \xrightarrow{THF} (C_5H_5)_2TiCl_2 + [MCl(SEt)_2]?$$

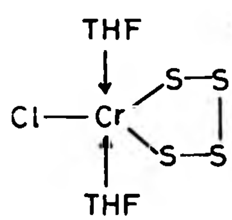
The one exception we found involved $CrCl_3$. A 1:1 reaction mixture followed the sequence above, $(C_5H_5)_2TiCl_2$ being isolated, when the molar proportions were 1:1.5 ($(C_5H_5)_2Ti(SEt)_2$: $[CrCl_3(THF)_3]$) no $(C_5H_5)_2TiCl_2$ was obtained. This reaction will be dealt with separately, at the end of the chapter. The reactions of $(C_5H_5)_2Ti(SEt)_2$ with $TiCl_4$, Me_2SnCl_2 and $Fe_2(CO)_9$ have also been studied. Before discussing a general reaction scheme, each will be dealt with in turn.

6i and 6ii With titanium (III) chloride tris (tetrahydrofuran) and with vanadium (III) chloride tris (tetrahydrofuran).

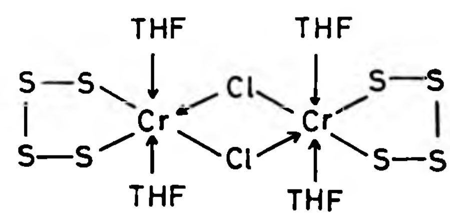
In both cases, $(C_5H_5)_2TiCl_2$ was isolated and identified but the second, tervalent metal species could not be obtained in a pure state and remain unidentified. In the Ti(III) case, separation of the $(C_5H_5)_2TiCl_2$ from the product mixture always lead to complete decomposition of the Ti(III) component. A brown solid (I) was obtained in the V(III) system, on removal of $(C_5H_5)_2TiCl_2$ by extraction with toluene or Et_2O. However i.r. data indicates some hydrolysis and attempted purification of the product was unsuccessful. The data obtained for the impure product does suggest the presence of coordinated THF, the i.r. band at $1010cm^{-1}$ being assigned to ν(C-O-C).

6iiia With chromium (III) chloride tris (tetrahydrofuran).

In this reaction, of a 1:1 mixture of $CrCl_3(THF)_3$ and $(C_5H_5)_2Ti(SEt)_2$, $(C_5H_5)_2TiCl_2$ was again obtained. A second product was also obtained, chemical analysis suggests the stiochiometry $[CrClS_4(THF)_2]$. Infra-red and ^{1}H.N.M.R. data confirms the presence of coordinated THF, the latter consists of two broad resonances (1.75(1) and 3.64(1) δ ppm) consistent with the presence of a paramagnetic metal ion (Cr(III)). The type of structure envisaged is one that includes a (CrS_4) heterocycle, eg (G) or (H).



G



H

A series of bands are observed in the low infra-red region (392(s) 338(s) 330(vs,sh) 320(s,sh) 305(s) and 280(m) cm^{-1}) attributable to (Cr-Cl) and (Cr-S) stretching modes. In the polymeric $[Cr(SEt)_3]$ formulation, i.r. absorptions at 490, 383, and $328cm^{-1}$ were assigned to ν(Cr-S) modes.[413] For comparison $[(C_5H_5)_2MoS_4]$, which contains a five-membered (MoS_4) ring, exhibits an i.r. band at $482cm^{-1}$ assigned tentatively to a S_4 skeletal vibration.[333] No such band was observed for our Cr(III) complex.

6iv and 6v With titanium (IV) chloride and titanium (IV)-chloride bis(acetonitrile).

Again evidence for ligand exchange was found, with the isolation of $(C_5H_5)_2TiCl_2$ in both cases. When the reaction was carried out on a non-coordinating solvent (benzene), Et_2S was also identified but no other products. This seems to indicate some further reaction, eg(b):-

a) $(C_5H_5)_2Ti(SEt)_2 + TiCl_4 \longrightarrow (C_5H_5)_2TiCl_2 + [Cl_2Ti(SEt)_2]$

b) $[Cl_2Ti(SEt)_2] \longrightarrow Cl_2TiS + Et_2S$

In a coordinating solvent (MeCN) a second product was isolated but was not fully characterized. Infra-red data and chemical analysis indicate the presence of coordinated MeCN, but some hydrolysis seems to have occurred .

Difficulty has been experienced in the preparation of $Ti(SR)_4$ compounds, intractable mixtures being obtained.[414] A possible route might be reaction of $TiCl_4$ with excess $(C_5H_5)_2Ti(SR)_2$ eg.$2(C_5H_5)_2Ti(SEt)_2 + TiCl_4 \longrightarrow (C_5H_5)_2 + Ti(SEt)_4$

6vi With dimethyl tin (IV) chloride

In this system $(C_5H_5)_2TiCl_2$ and Et_2S,were isolated, a Sn(IV) component was not located. This seems surprising at first sight, the expected products from the reaction being $Me_2Sn(SEt)_2$ and $(C_5H_5)_2TiCl_2$, however it seems that fractional distillation of the volatile products lead to decomposition of the $Me_2Sn(SEt)_2$:-

$$Me_2Sn(SEt)_2 \longrightarrow \frac{1}{3}(Me_2SnS)_3 + Et_2S$$

as known to occur in the case of the phenyl analogue.[415] The $(Me_2SnS)_3$ may have been lost by sublimation.

6vii With diiron enneacarbonyl.

Again ligand exchange is found to occur, in this case $[Fe_2(CO)_6(SEt)_2]$ was obtained. The titanium fragment could not be identified, but no evidence for the formation of $(C_5H_5)_2Ti(CO)_2$ was found:-

$$(C_5H_5)_2Ti(SEt)_2 + Fe_2(CO)_9 \longrightarrow Fe_2(CO)_6(SEt)_2 + (C_5H_5)_2Ti?$$

This is in complete contrast to the reactions of $(C_5H_5)_2Ti(SR)_2$ compounds with the mononuclear carbonyls $[(nor\text{-}C_7H_8)M(CO)_4]$ (M=Cr, Mo,W) described in the introduction to this chapter.

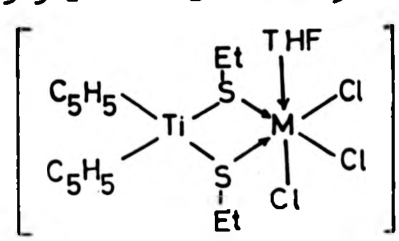
General observations on the reactions studied.

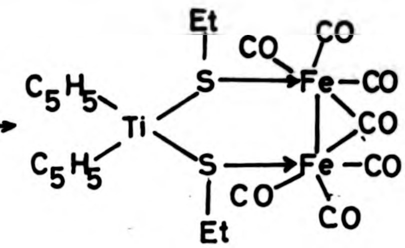
Although the reactions studied represent the start of this programme, it is clear that ligand exchange occurs readily. Consequently these particular systems do not provide a route to the desired mixed-valence species. We do propose, however, that binuclear species are formed initially prior to ligand exchange.

Considering a possible reaction scheme, the first step is therefore, seen as the formation of binuclear species via the sulphur atoms of the thiolate groups:-

eg.

a) $(C_5H_5)_2Ti(SEt)_2 + MCl_3.(THF)_3 \longrightarrow$



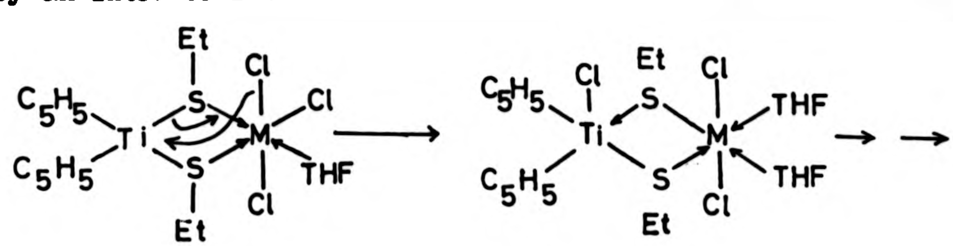
b) $(C_5H_5)_2Ti(SEt)_2$ + $Fe_2(CO)_9$ ⟶ 

Now the sulphur atoms in many thiolate complexes have been shown to be fairly sensitive to electrophilic attack. Thus $(C_5H_5)_2TiCl_2$ is formed by reaction of $(C_5H_5)_2Ti(SEt)_2$ with $PhCH_2COCl$.[416] Similarly $(C_5H_5)_2M(SR)_2$(M=Mo,W,R=Me,Et) complexes react readily with concentrated HCl, giving the dichloride and RSM.[417] Most metal thiolate complexes react with alkyl-halides to give products in which S-alkylation of the coordinated thiolate group has occurred.[418] The resulting dialkylsulphide may (a) or may not (b) be coordinated to the metal depending on donor strength:-

a) $Pt(SR)_2$ + $RI \longrightarrow PtI_2(SR_2)_2$

b) $RHg(SR)$ + $R'Cl \longrightarrow RHgCl$ + RSR'

The next step in the reaction scheme is, thus seen as breakdown of the binuclear complex via ligand exchange, either by an intra-or inter-molecular mechanism:-



$[ClM(SEt)_2(THF)_3]$ + $(C_5H_5)_2TiCl_2$

The variety of reaction products noted for the different system is seen as resulting from the decomposition of the bis(ethanethiolato) metal halide species. Where $(C_5H_5)_2TiCl_2$ is formed it is very easily isolated and identified. However the method of its removal may be the main cause of the decomposition of the other products, which would be expected to be highly unstable with respect to hydrolysis and oxidation.

Consider the reaction system; $(C_5H_5)_2Ti(SEt)_2$ + $CrCl_3(THF)_3$; where the green product (II), thought to contain a (CrS_4) heterocycle, was obtained. Though formation of a product of this type is not obvious, similar behaviour has been noted, eg the reaction of $(C_5H_5)_2Ti(SH)_2$ with iodine does not give the expected disulphide but $(C_5H_5)_2TiS_5$.[331] This was explained in terms of the instability of the smaller rings (TiS_x) (x=2,3,4) compared to the (TiS_5) ring. With $TiCl_4$, in a non-coordinating solvent, Et_2S was identified, indicating the possible decomposition:-

$$[Cl_2Ti(SEt)_2] \longrightarrow Cl_2TiS \quad + \quad Et_2S$$

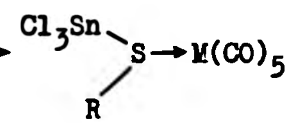
however no species of the type $[Cl_2TiS]$ could be identified. Previous work described in chapter 5, where $[Cl_2TiS]_n$ and its adducts $[Cl_2TiS.3L]$ (L=MeCN or THF) were prepared, leads us to believe that if any of this compound had been obtained initially, it must have hydrolysed on work up.

If the reaction is carried out in a coordinating solvent eg. MeCN, the product appears to be stabilized via solvent coordination, as no Et_2S was obtained:-

$$(C_5H_5)_2Ti(SEt)_2 + TiCl_4(MeCN)_2 \rightarrow (C_5H_5)_2TiCl_2 + Cl_2Ti(SEt)_2(MeCN$$

The behaviour of $(C_5H_5)_2Ti(SEt)_2$ as described in this chapter closely parallels that of the similar (alkanethiolato) tin(IV) halides. These (alkanethiolato) tin (IV) compounds have also been shown to undergo two distinct reactions:-

a) with binary metal carbonyls ligand substitution may occur, with donation via the sulphur atom:-[397]

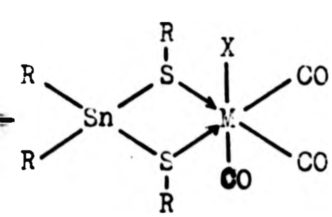
$Cl_3Sn(SR) + M(CO)_6 \longrightarrow$ 

b) with metal- and alkyl-halides fission of the tin-sulphur bond may occur:-[419-425]

$$R_2Sn(SMe)_2 + xsMeI \longrightarrow R_2SnI_2 + 2Me_3S^+I^-$$

Reaction of $R_2Sn(SR')_2$ compounds with pentacarbonyl metal halides gives good yields of the trimeric species $[M(CO)_3(SR')]_3$.[419,422]

The mechanism postulated involved the formation of an intermediate substitution product:-

$M(CO)_5X + R_2Sn(SR')_2 \longrightarrow$ 

Fission of a (Sn-S) bond, either by intra- or inter-molecular elimination then gives monomeric $[M(CO)_3(SR')]$ units which subsequently trimerise.

6iiib With chromium (III) chloride tris(tetrahydrofuran).

In a second case, a 1:1.5 mixture of $(C_5H_5)_2Ti(SEt)_2$ and $CrCl_3(THF)_3$ gave only one product, a blue solid (III), no $(C_5H_5)_2TiCl_2$ being isolated. This blue solid gave a low sulphur analysis and no evidence for the presence of any cyclopentadienyl groups could be found in either the infra-red or ^{1}H.N.M.R. spectra of the product. The electronic spectrum of the complex exhibits a very intense absorption at 15152cm^{-1} with a less intense band at 19152 cm^{-1}, c.f.$(C_5H_5)_2Ti(SEt)_2$ absorbs at 18,690 cm^{-1}. The loss of cyclopentadienyl groups from a system such as this is not unknown, for example $(C_5H_5)_2TiCl_2$ gives $[(C_5H_5)TiCl(O)]_4$ on hydrolysis [322] and $[(C_5H_5)TiCl(OEt)_2]$ on treatment with EtOH.[426,427]
This and the inclusive analytical data makes speculation as to the course of this reaction impossible.

CHAPTER SEVEN.

THIOUREA COMPLEXES OF THE GROUP VB TRIHALIDES.

INTRODUCTION

This study arises from collaboration with the university of Nairobi, concerning the use of sulphur bonded antimony complexes as possible schistosomicides.[428] Despite toxic side effects, antimony compounds have been used for many years in the treatment of schistosomiasis [429] and leishmaniasis.[430] An evaluation of the nature and extent of the toxic effects and the chemistry of these Sb-S systems, with a correlation between the two is required. This work sets out to investigate the chemistry of the thiourea~antimony system by looking at the general thiourea /ECl_3 (E=P,As,Sb,Bi) systems.

There is a significant change in the behaviour of the group VB trihalides progressing down the group from phosphorus to bismuth. Compounds of the type EX_3(E=P,As,Sb,Bi, X =Halogen, R,H etc) are capable of both donor and acceptor properties, the electrons from the lone pair on E(III) may donate to suitable acceptor molecules, or the element E may expand its coordination number by accepting electrons from donor molecules. The former behaviour is predominant with P(III) compounds, whilst with Sb(III) and Bi(III), the latter is more common.

Phosphorus (III) compounds are strong Lewis bases and innumerable complexes are known where they act as donors to a host of different metal centres.[431] Complexes where P(III) halides act as acceptors are extremely rare since they are weak Lewis acids. Of the few examples known, there is a tendency to dissociate at temperatures above the low temperatures used for their formation.[432] The donor strength decreases in the series $PX_3 > AsX_3 > SbX_3 > BiX_3$ and whilst As (III) compounds behave as donors in many complexes this behaviour is not typical for Sb(III) and Bi(III) compounds. Although Sb(III) compounds have been found to react with a variety of transition-metal carbonyls,[433] even $SbCl_3$,[434] no similar behaviour has been noted for Bi(III) halides. In contrast Sb(III) and Bi(III) halides form a wide range of complexes EX_3L_n (L= mono- or polydentate ligands, n varies) where they act as Lewis acids.[435,436]

Structurally, the halide complexes are of interest because of the part played by the lone pair in determining the stereochemistry. In 1:1 (MX_3 : monodentate ligand) complexes the lone pair occupies an equatorial position in a trigonal bipyramidal configuration with the donor in an axial position, eg. $[SbCl_3(PhNH_2)]$.[437] In 1:2 complexes the lone pair occupies an octahedral position, so that a distorted square pyramidal environment for the antimony results eg. $[SbCl_3(Ph_3AsO)_2]$.[438] Crystal structure determinations have shown that octahedral six-fold coordination occurs in $[AsCl_3(bipy)]_2$;[439] $[SbCl_4]^-$ $(C_5H_5NH)^+$;[440] $[Sb_2Br_9]^{3-}.5(C_5H_5NH)^+ . 2Br^-$;[441] $[BiBr_4]^-$ (2-picolinium)$^+$[442]; and $[BiBr_6]^{3-}$ — $(Me_2NH_2)^+{}_3$,[443] via halogen bridging, with the lone pair stereochemically inactive. Similar structures were inferred, from i.r. data, for $[MCl_3(bipy)]$ (M=Sb,Bi) but the analogous bromide and iodide complexes were thought to be mononuclear[444]

The tridentate ligand, terpyridyl, serves to illustrate the differences in the coordination behaviour of the elements in the group. The ratios, MX_3: terpy, vary, the As(III) compounds are 1:1 electrolytes in nitrobenzene, the antimony complexes 2:1 electrolytes and $BiCl_3$(terpy) is essentially a non-electrolyte (Table 7.1).[442]

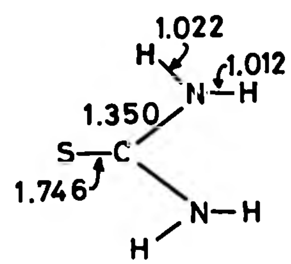
Table 7.1 Terpyridyl complexes of Arsenic (III), Antimony (III) and Bismuth (III) halides.

Compound	Λ_m^a ($ohm^{-1}mol^{-1}cm^2$)	Probable Formulation
$2AsCl_3$.terpy	28.1	$[AsCl_2(terpy)]^+(AsCl_4)^-$
$AsBr_3$.terpy	24.3	$[AsBr_2(terpy)]^+Br^-$
$3SbCl_3$.2terpy	41.1	$[SbCl_2(terpy)]_2^+(SbCl_5)^{2-}$
$3SbBr_3$.2terpy	35.8	$[SbBr_2(terpy)]_2^+(SbBr_5)^{2-}$
$BiCl_3$.terpy	5.7^b	

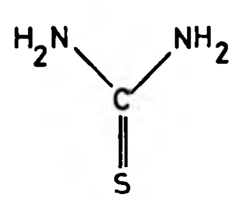
a: In nitrobenzene, in which a 1:1 electrolyte gives Λ_m 20–30.

b: Insoluble in nitrobenzene, Λ_m in DMF.

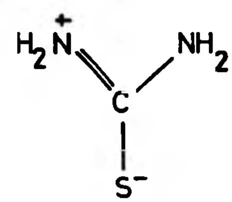
Thiourea is a planar molecule, with the hydrogen atoms basically coplanar with the (SCNN) group (A).



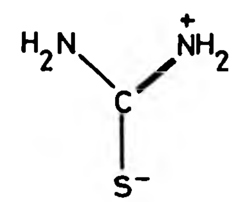
Hydrogen bonding occurs between both hydrogens and the sulphur atom, N—H·····S.[445,446] Overlap of the lone pair of electrons on the nitrogen atoms with the p-orbital of the carbon atom may be envisaged, giving rise to the resonance structures (C) and (D).[447]



B



C



D

The more polar solvents will favour the charge separated structures, and hence formation of donor-acceptor complexes coordinated via the sulphur atom. For instance, if thiourea and iodine are mixed in a 2:1 molar ratio in $CHCl_3$, a yellow crystalline complex (E) can be isolated.

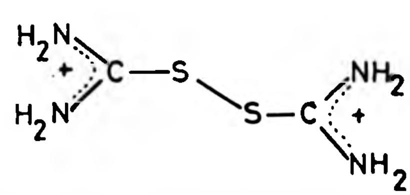
$$[(H_2N)_2C{=}S \longrightarrow I \longleftarrow S{=}C(NH_2)_2]^+I^-$$

E

In a more ionizing solvent oxidation of the thiourea occurs:-[449]

$$(H_2N)_2C{=}S + I_2 \longrightarrow [(H_2N)_2C\text{-}S\text{-}S\text{-}C(NH_2)_2]^{2+}.2I^-$$

The positive charge maybe envisaged as spread over the amino group (F).



F

Thiourea and its N- substituted derivatives,form complexes with a diverse range of metals, from potassium to platinum.[450] Coordination may occur through the nitrogen atoms[451-454] as well as via the sulphur atoms,[455-464] although the latter is the more common. Nitrogen coordination is expected with "hard" Lewis acids, as found in $TiCl_4(tu)_2$[465], although both nitrogen and sulphur donation has been noted with $SnCl_4$.[452,465] The majority of thiourea complexes involve sulphur donation, those of the 2nd and 3rd row transition metals[467,468] being very stable. With 1st row transition elements the complexes tend to dissociate in solution indicating only weak ($M \leftarrow S$) bonding

The structures of a number of thiourea complexes have been determined, and are varied, depending on the central metal atom. In $NiCl_2(tu)_4$ the nickel is octahedral[469], similarly in $Ni(NCS)_2(tu)_2$ where each thiourea is bound to two nickel atoms giving a polymeric structure.[470] In the former complex the (S-C) distance is abnormally long (1.77Å) compared to thioiurea itself (1.64Å).[469,471] The complex $CdCl_2(tu)_2$ is tetrahedral and $PbCl_2(tu)_2$ is polymeric with seven-coordinate lead via four bridging sulphur atoms and two bridging chlorines.[469]

EXPERIMENTAL.

The antimony and bismuth complexes were air stable, however with the phosphorus and arsenic complexes decomposition occured on exposure to air and consequently were handled either in the dry box or on the vacuum line.

Thiourea is a cancer suspect agent and care was taken in the handling of this material.

Reactions of thiourea :-

7i With bismuth (III) chloride.

Thiourea (4g; 52.5mmols), dissolved in acetone (~250cm^3), was added to a warm solution of $BiCl_3$(3.2g; 10.0mmols) in acetone (~50cm^3). The yellow solid (I) deposited immediately was collected by filtration and recrystallised from hot acetone/methanol. The solid turned deep red on drying under vacuum overnight (3.2g; 59% ; mpt >428 dec.)

Infra-red Data (cm^{-1};nujol and H.C.B. mulls) 3430(s) 3385(s) 3270(m) 3180(s) 3120(m,sh) 1645(m,sh) 1620(vs) 1600(s) 1550(m,sh) 1415(m) 1390(s,sh) 1380(s) 1160(w,br) 1090(w,br) 1035(w) 730(w) 715(m,sh) 700(s) 675(w) 605(m) 530(s,br) 490(s) 475(s) 460(s) 390(vw) 360(vw) 171(s) 154(m).

^{1}H.N.M.R. Data (δ ppm; ref TMS; d^6 DMSO solution) 7.010 (br)

^{13}C.N.M.R. Data (δppm; ref TMS; d^6 DMSO solution) 181.74.

Chemical Analysis (%) Found, C: 6.92, H:2.23, N:15.42, S: 17.98, Calc'd for $C_3H_{12}N_6S_3BiCl_3$ C: 6.67, H: 2.24, N: 15.51, S: 17.79.

7ii With Antimony (III) chloride in acetone.

Thiourea (8.9g; 116.9 mmols), dissolved in acetone

(~200cm^3), was slowly added to $SbCl_3$(6.7g; 29.4mmols) in ~50cm^3 acetone. A lime coloured solution developed from which a pale yellow solid deposited on standing overnight. The product was recrystallised from MeCN as lemon coloured srystals (II) (8.8g; 74%; mpt >379K dec.)

<u>Infra-red Data</u> (cm^{-1}; nujol and H.C.B. Mulls) 3340(s) 3280(s) 3185(s) 3130(s) 1635(s,br) 1515(m) 1500(w) 1425(s) 1390(s) 1365(m,sh) 1175(w,br) 1110(w) 1065(w) 1000(m) 725(m,sh) 715(m) 620(w) 575(w) 475(s) 412(w) 360(vw) 307(s) 145(w,br)

<u>^{1}H.N.M.R. Data</u> (δ ppm; ref TMS; d^6DMSO solution) 6.94(br).

<u>^{13}C.N.M.R. Data</u> (δ ppm; ref TMS; d^6DMSO solution) 182.00

<u>Chemical Analysis</u> (%) Found, C:6.41, H:2.59, N:15.63, S:18.92, Cl:25.72, Calc'd for $C_7H_{28}N_{14}S_7Sb_3Cl_9$, C:6.91, H:2.32, N:16.11, S:18.40, Cl:26.20.

<u>7iii With antimony (III) chloride in the presence of dimethylformamide.</u>

$SbCl_3$(10g; 43.48 mmols) was dissolved in DMF (~25cm^3) then the volume made up to ~250cm^3 with benzene. This solution was slowly added to a DMF solution of thiourea (10.5g;137.90mmols) giving a yellow solution on complete addition. Concentration of the solution followed by dropwise addition of Et_2O caused precipitation of a yellow solid (III). The product was recrystallised from MeCN (14.5g; 73%; mpt 356-358K).

Controlled heating of this yellow product under vacuo at 348K, followed by extraction and recrystallization from MeCN gave a yellow-orange product (IV); identical to the product (II) obtained in 7ii.

Yellow Solid (III).

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 3315(s) 3265(s) 3160(s) 3100(s) 3070(s,sh) 2960(m,sh) 2920(m,sh) 2860(m,sh) 2710(w) 2660(m) 1630(vs,br) 1515(m) 1428(s) 1390(s) 1250(w) 1100(w) 705(m) 660(m) 630(m) 575(m) 470(m) 408(w) 380(vw) 316(m) 237(w,br) 192(s) 145(w)

^{1}H.N.M.R. Data (δ ppm;ref TMS; d^{6}DMSO solution) 2.72 (3) 2.88 (3) 7.04 (8,br) 7.94 (1)

^{13}C.N.M.R. Data (δ ppm; ref TMS; d^{6}DMSO solution) 36.09, 182.85

Chemical Analysis (%) Found, C:12.39, H:3.04, N:15.76, Cl:23.60, Calc'd for $C_5H_{15}N_5OS_2SbCl_3$, C:13.24, H:3.33, N:15.44, Cl:23.46,

Orange-yellow solid (IV)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 3320(s) 3240(s) 3140(s) 3080(s) 1620(vs,br) 1500(vw) 1450(vw) 1410(w) 1365(m,br) 1135(w) 1075(w) 1015(w) 965(w) 910(w) 845(w) 790(w) 720(m) 700(m) 660(m,sh) 610(m) 540(w) 455(m) 400(m,sh) 318(m) 218(w,br) 181(s) 158(m,br)

^{1}H.N.M.R. Data (δ ppm; ref TMS; d^{6}DMSO solution) 7.057 (br)

^{13}C.N.M.R. Data (δ ppm; ref TMS; d^{6}DMSO solution) 183.241

Chemical Analysis (%) Found, C:8.86, H:2.90, N:16.10, Cl:27.73, Calc'd for $C_7H_{28}N_{14}S_7Sb_3Cl_9$, C:6.91, H:2.32, N:16.11, Cl:26.20.

7iv With arsenic (III) chloride in acetone.

$AsCl_3$(7.9g; 43.6mmols), dissolved in acetone (~20cm^3) was added to an acetone (~200cm^3) solution of thiourea

(10g: 131.4mmols). The white solid (V) which slowly precipitated from the resulting yellow solution was filtered and washed sequentially with acetone, benzene and n-hexane. The product (14.4g; 62%, mpt 411-413K) was dried in vacuo at R.T.

Infra-red Data (cm^{-1}; nujol and H.C.B.mulls) 3360(s) 3280(s,br) 3180(s) 3100(s,br) 1665(s,sh) 1655(vs) 1625(s,sh) 1600(m,sh) 1482(w) 1425(m) 1405(m) 1390(m) 1370(m,sh) 1030(w) 718(m) 700(m) 640(m,br) 575(s) 475(w) 450(w) 400(vw) 315(w) 285(w)

^{1}H.N.M.R. Data (δ ppm; ref TMS; d^6DMSO solution) 9.84(br)

Chemical Analysis (%) Found, C:8.96, H:3.06, N:20.46, Cl:26.44, Calc'd for $C_3H_{12}N_6S_3AsCl_3$, C:8.80, H:2.95, N:20.52, Cl:25.97.

7v With arsenic (III) chloride in dimethylsulphoxide.

$AsCl_3$($5cm^3$;59.58mmols), dissolved in benzene (150 cm^3), was slowly added to a DMSO ($200cm^3$) solution of thiourea (14.0g;183.92 mmols). The white precipitate (VI) formed, was collected by filtration, washed with benzene and n-hexane and dried in vacuo (22.7g;81%, mpt 404-405K)

Infra-red Data (cm^{-1}; nujol and H.C.B. mulls) 3340(s,sh) 3290(m,sh) 3230(s) 3140(s) 2950(s,sh) 2910(s) 2860(s,sh) 2720(m,sh) 1650(vs) 1595(m,sh) 1480(m) 1425(m,sh) 1395(s,br) 1310(m) 1110(w) 1080(m) 1050(s,sh) 1015(vs) 950(vs) 935(s,sh) 900(w) 780(m,sh) 730(m,sh) 705(s) 665(m,br) 610(m) 470(s) 380(m) 335(m)

^{1}H.N.M.R. Data (δ ppm; ref TMS; d^6DMSO solution) 6.05 (1,br) 9.76 (1,br) (D_2O solution) 2.256

^{13}C.N.M.R. Data (δ ppm; ref TMS; D_2O solution) 39.712, 167.234.

Chemical Analysis (%) Found, C,16.97, H:4.52, N:13.53, Cl: 17.4 (uncertain end point), Calc'd for $C_9H_{30}N_6O_3S_6AsCl_3$, C:16.79, H:4.70, N:13.05, Cl:16.51.

7vi With phosphorus (III) chloride.

A benzene solution (~25cm^3) of PCl_3 (6.0g; 43.71 mmols) was added dropwise to a solution of thiourea (10.0g; 131.4mmols) in 1:1 DMF/ benzene (~100cm^3). Overnight a white solid separated from the yellow solution, which was collected by filiration and then recrystallised from DMF/Et_2O as white needles (VII) (4.4g;28%; mpt 467-470K). Concentration of the filtrate lead to precipitation of a yellow solid identified as sulphur (0.67g; 16% based on thiourea).

Infra-red Data (cm^{-1};nujol and H.C.B. mulls) 3340(m,sh) 3260(s) 3200(m) 3100(s) 3040(s) 2940(s,sh) 2880(s) 2820(s,sh 2820(s,sh) 2740(m,sh) 1740(s,br) 1676(s,br) 1605(s) 1510(s) 1460(m) 1445(m) 1410(m) 1340(w) 1300(s) 1260(w) 1240(w) 1150(w) 1130(w) 1060(w) 1020(w) 975(m) 850(m) 790(w) 760(s) 713(s) 652(m) 610(s) 550(s) 480(w) 435(s) 390(w) 200(m) 178(s) 136(w)

^{1}H.N.M.R. Data (δ ppm; ref TMS; d^{6}DMSO solution) 3.269 (3) 3.367 (3) 7.656 (2,br) 8.674 (1)

^{13}C.N.M.R. Data (δ ppm; ref TMS; d^{6}DMSO solution) 155.93, 153.73, 44.02.

^{31}P.N.M.R. Data (δ ppm; ref H_3PO_4; d^{6}DMSO solution) 2.180

Chemical Analysis (%) Found, C:23.78, H:4.83, N:15.49, Cl:29.26, Calc'd for $C_7H_{18}N_4O_2SCl_3P$, C:23.37, H:5.04, N:15.58, Cl:29.57.

DISCUSSION

As in other studies of related systems, infra-red evidence forms the basic analytical tool for diagnostic evaluation of the mode of coordination. X-ray analysis to give unequivocal molecular structures being limited to systems in which suitable crystals are obtained. Thus a short description of the several characteristic infra-red bands of thiourea follows.

Jensen and Nielsen [472] have assigned a number of characteristic vibrational modes by studying a large number of thioamides, selenoamides, thioureas and selenoureas. The bands are designated by letters A to G.

The A band - generally found in the region 1600-1650 cm^{-1} in the spectra of all thioamides, selenoamides, thioureas and selenoureas containing an unsubstituted NH_2 group, it orginates from NH_2 deformations but is coupled with the (C-N) stretching vibration. On complex formation via the S or Se atom, it shifts to higher frequency.

The B band - a strong band in the range 1400-1600 cm^{-1}. In thio- and selenoureas it is thought to arise chiefly from the ν_{as}(N-C-N) mode, with possibly some coupling to the CS (or CSe) and the (NH) and NH_2 vibrational modes.

The C band - a medium to strong band appearing in the 1200-1400 cm^{-1} region, although it may occur at slightly higher frequency eg. thiourea; 1415 cm^{-1}. In thio- and selenoureas it has been assigned to the (N-C-N) grouping, in substituted derivatives mixing with the NH vibrations may occur.

The D band - 1000-1200 cm^{-1} range, of medium strength. Not observed in symmetrically disubstituted aromatic thioureas. Mainly due to the symmetrical stretching mode of the (N-C-S) grouping, extensive coupling with NH vibrations occur in compounds with a N-alkyl or N,N dialkyl thioamide group.

The E band - a characteristic band, usually in the range 800-900 cm^{-1}. The main contribution is assigned to NH_2 bending, but may be absent in primary thioamides due to coupling with other vibrations. On complex formation it is often- weakened and is sometimes completely missing.

The F band - a band near 700 cm^{-1}, typical for most thioamides and thioureas. It is assigned to NH vibrations, with perhaps contributions from (C=S) modes.

The G band - the only band to show a significant shift on going from the thio- to the seleno-compounds. It is therefore assigned to ν(C-S) or ν(C-Se). In the thio compounds it is found in the range usually cited for single bond ν(C-S) (600-800 cm^{-1}). For the seleno analogues it occurs 30 to 100cm^{-1} lower.

Infra-red spectra of thiourea and its metal complexes.

Changes in the spectrum of thiourea on S - protonation, S - methylation and on complex formation supports the view that the B,C and D bands have their origin in the ν_{as} (N-C-S), ν(N-C-N) and ν_s(N-C-S) vibrations, respectively (Table 7.2).

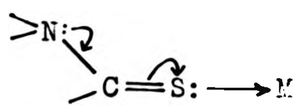
There has been some disagreement on the position of the (C-S) stretching frequency, assignments have ranged from 1413 cm^{-1} [447], to 1086 cm^{-1} [473] through to 629 cm^{-1} [472].

Table 7.2 Infra-red absorption bands of thiourea and substituted thioureas and their metal complexes (as assigned by Jensen and Nielsen[472]).

Compound	Infra-red absorptions (cm^{-1})						
	A	B	C	D	E	F	G
Thiourea	1612	1473	1413	1086		727	629
$Pt(tu)_4Cl_2$	1605 1625	1504	1385 1425	1080		706	637 562
$Cu(tu)_3Cl$	1610 1635	1500	1385 1420	1090		706	530
N-Methylthiourea	1627	1550	1257	1125	777	719	625
$Pt(Metu)_4\ Cl_2$	1617 1635	1569	1245 1285	1125 1145	763 773	713	607 637
N-Ethylthiourea	1625	1548 1567	1267 1308	1112 1130	807	740	644
$Pt(Ettu)_4\ Cl_2$	1627	1562 1582	1267 1303	1123	790	743	628

Yamaguchi et al [451,457] proposed that bands at 1417, 1083 and 730 cm^{-1} all contain contributions from modes associated with the C=S group. Thus coordination via the sulphur atom will shift all these bands to lower frequency. In the case of the 1083cm^{-1} band (the D band) there is also a large contribution from the ν(N-C-N) mode, the frequency of which will shift to higher frequency on complexation via the sulphur and therefore the contribution to it from the (C=S) vibration is reduced. Thus the overall effect is a reduction in intensity of this band on complex formation. The composite F (730 cm^{-1}) and

G (629cm^{-1}) bands shift to lower energy corresponding to a weakening of the C=S bond. Bands involving the ν(N-C-N) mode, B (1473cm^{-1}) and C (1413cm^{-1}), are shifted to higher frequency reflecting the increase in the double bond character of the (C-N) linkage (F).



F

The intense ν(N-H) bands in the 3100- 3400 cm^{-1} region remain virtually unchanged. In contrast on coordination via the nitrogen atoms these bands exhibit marked negative shifts [451,452]. The B band also shows a distinct change on N-donation, becoming more intense and shifting to slightly lower frequency.

For simplicity each reaction will now be discussed in turn, possible structures being proposed for the resulting products. Their biological application vis-a-vis utilisation as schistosomicides is under investigation.

Reactions of Thiourea:

7i With bismuth (III) chloride.

During the completion of this work, the crystal structures of the bismuth (III) complexes - $[Bi_3Cl_9(tu)_7]$ [474] and $[BiCl_3(tu)_3]$[475] were published. Both the yellow, 3:7, and red, 1:3, complexes contain two kinds of chemically non-equivalent Bi(III) atoms, which are octahedrally surrounded by chloride ions and/or thiourea molecules. The former (Fig7.1), di-μ-chlorobis [chloro tris (thiourea) bismuth (III)] pentachloro (thiourea) bismuthate(III), contains a binuclear cation with bridging chlorine atoms, the anion is disordered.

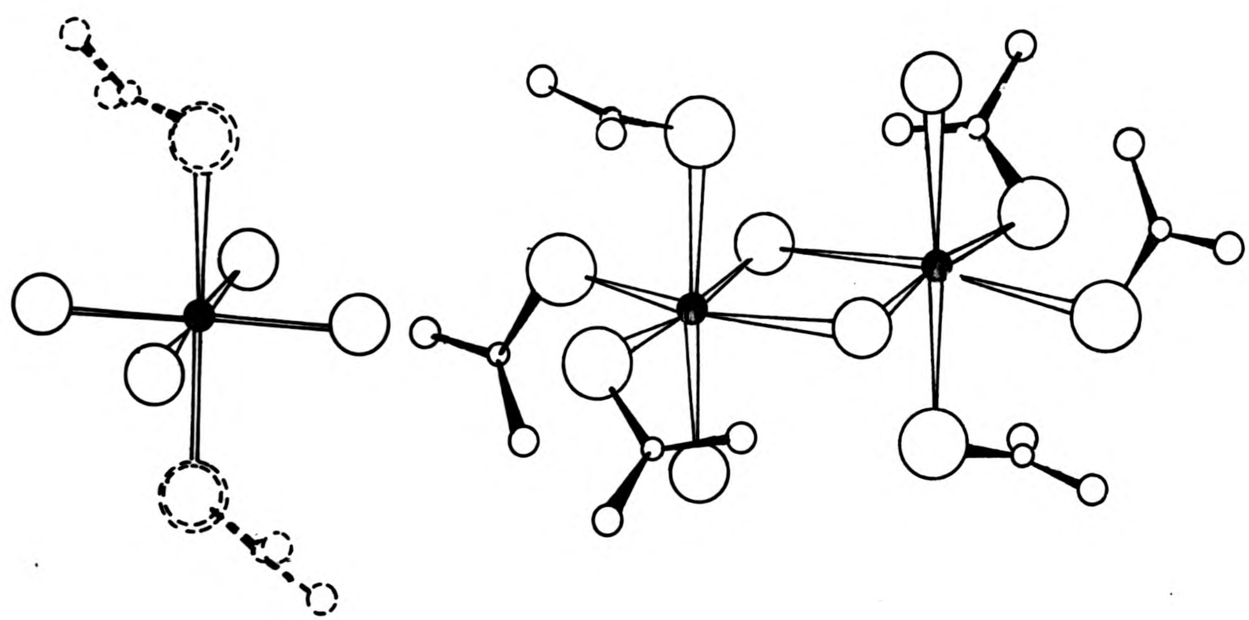


Fig. 7.1. Crystal structure of di-μ-chloro-bis[chloro tri(thiourea) bismuth(III)] penta chloro(thiourea) bismuthate (III).

The 1:3 complex (Fig 7.2) - $[Bi(tu)_6][Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]_2$, also contains a disordered anion but this disorder involves three chloride ions and three thiourea molecules, so the anion is either $[BiCl_6]^{3-}$ or $[BiCl_3(tu)_3]$ In both complexes the lone pair is stereochemically inactive, this is not particularly unusual, as many complexes have structures of this type.[476] A third complex - $Bi_2Cl_6(tu)_3$ - has also been discussed,[477] but little data is available.

In contrast to these ionic complexes, the ethylene thiourea (etu) adduct - $[BiCl_3(etu)_2]$ consists of polymeric chains. The coordination at Bi(III) is octahedral involving two etu molecules and four chloride ions, two of them bridging adjacent Bi(III) atoms forming infinite zig-zag chains.

Reaction of thiourea and $BiCl_3$ in acetone yields the complex (I) which was initially yellow but turned red on drying overnight under vacuum. Analysis of the solid indicated the stiochiometry $[BiCl_3(tu)_3]$ and this presumably corresponds to the red 1:3 complex characterized structurally by Battaglia et al.[475] Infra-red data is consistent with sulphur donation (Table 7.3), giving a high energy shift in the B (1505cm^{-1}) and C (1435cm^{-1}) bands, and a low energy shift to the F (700cm^{-1}) and G (605cm^{-1}) bands. ^{1}H.N.M.R. (7.010 δ ppm) and ^{13}C.N.M.R. (181.74 δ ppm) data indicates the complex is dissociated in DMSO solution. This behaviour has been noted before in the Cr(III) and Ni(II) complexes of thiourea and substituted thioureas where the thiourea is only weakly bound to the metal centre.[453,463,464].

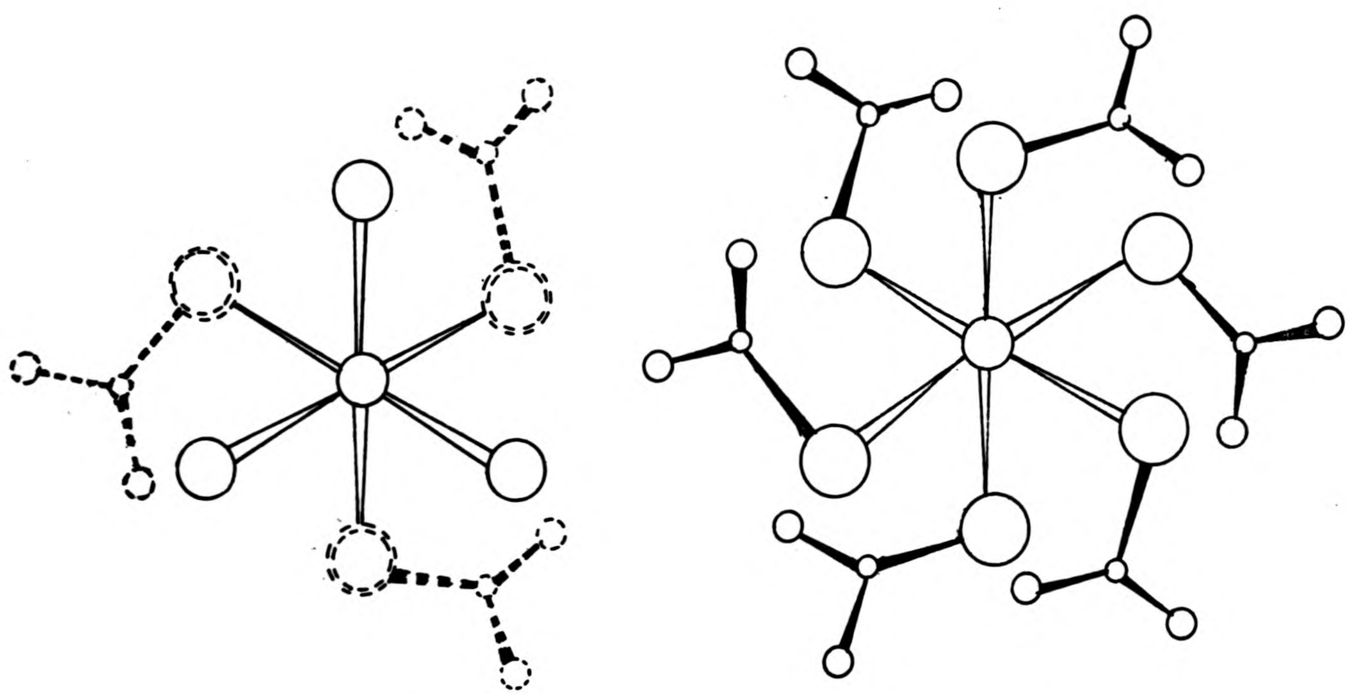


Fig. 7.2. Crystal structure of $[Bi(tu)_6][Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]_2$

Table 7.3 Important infra-red bands (cm^{-1}) of the thiourea complexes.

Complex	ν_{NH}	B	C	D	F	G
Thiourea	3365	1473	1413	1086	730	629
	3258					
	3156					
	3097					
$[BiCl_3(tu)_3]$ (I)	3430	1505	1435	1090	700	605
	3385					
	3270					
	3180					
$[Sb_3Cl_9(tu)_7]$ (II)	3340	1515	1425	1075	715	610
	3280					
	3185					
	3130					
$[SbCl_3(tu)_2(DMF)]$ (III)	3315	1515	1428	1073	705	610
	3265					
	3160					
	3100					
$[AsCl_3(tu)_3]$ (IV)	3360	1482	1425	1080	718	575
	3280					
	3180					
	3100					
$[AsCl_3(tu)_3(DMSO)_3]$ (V)	3340	1480	1422	1081	705	610
	3290					
	3230					
	3140					

Table 7.3 continued.

$PCl_3(tu)(DMF)_2$ (VI)	3260 3200 3100 3040	1460	1410	1090	760 713	610

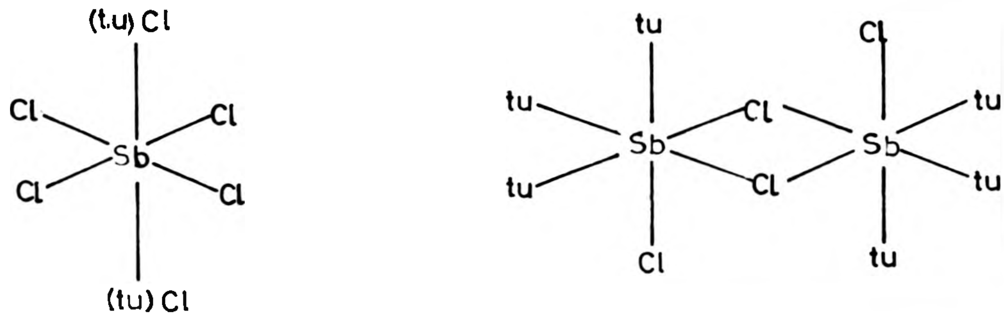
7iv With antimony (III) chloride in acetone.

$SbCl_3$ more closely resembles its bismuth (III) analogue than $AsCl_3$, and this is reflected in the products obtained on reaction with thiourea. When a 4:1 (tu:$SbCl_3$) ratio of reactants is mixed in acetone a lemon coloured product (II) is obtained which analyses as $[Sb_3Cl_9(tu)_7]$, rather than $[SbCl_3(tu)_3]$ for which no evidence of formation could be found in this system. ^{1}H.N.M.R. (6.94 δppm) and ^{13}C.N.M.R. (182.00 δppm) data indicate the complex to be dissociated in DMSO, since the resonances are little shifted from that of free thiourea. Solid state i.r. data show that the thiourea is coordinated through the sulphur in the solid state (Table 7.3) shown by the lowering of the frequency of the F and G bands and the shifts to high energy of the B and C bands. The structure envisaged (G) is analogous to that of the bismuth complex.

7iii With antimony (III) chloride in the presence of DMF.

The second $SbCl_3$/tu complex prepared was obtained from a DMF/benzene solution as yellow solid (III). It analyses as $[SbCl_3(tu)_2(DMF)]$, containing coordinated DMF as well as thiourea. The DMF could be removed by controlled heating in vacuum giving a yellow-orange solid (IV), which was identical to product

(II) analysing for [$Sb_3Cl_9(tu)_7$].

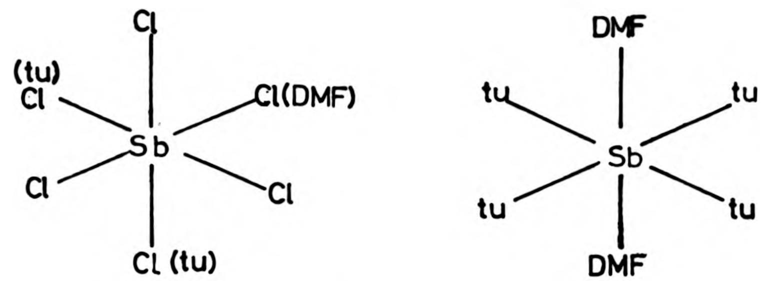


G

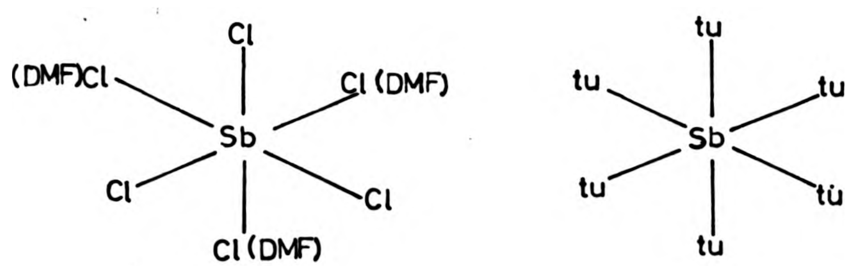
Infra-red evidence again indicates sulphur coordination (Table 7.3). Bands due to DMF can also be identified, in particular the band at 660 cm^{-1} is assigned to a (O-C-N) bending mode little shifted from that of free DMF ($657cm^{-1}$). The carbonyl stretching vibration of free DMF occurs at $1675cm^{-1}$, in our complex the band at $1630cm^{-1}$ is thought to contain contributions from this mode and also from the (N-H) bending mode of thiourea. For comparison in [$Sb(DMF)_6(ClO_4)_3$] ν(C-O) is found at $1667cm^{-1}$ and the (O-C-N) bending vibration at $670cm^{-1}$.

The product (III) is dissociated in DMSO solution as shown by the broad resonance (7.04 δ ppm) due to NH_2 protons of thiourea in its ^{1}H.N.M.R. spectrum and the peak (182.85 δ ppm) assigned to ^{13}C=S in its ^{13}C.N.M.R. spectrum, both of which are little shifted from uncoordinated thiourea. Resonances at 2.72, 2.88 and 7.94 δ ppm in its proton spectrum and at 36.09 δ ppm in its ^{13}C.N.M.R. spectrum confirm the presence of DMF.

A similar structure to that of the bismuth complex, $BiCl_3(tu)_3$, is envisaged for this complex (H) or (I).



H

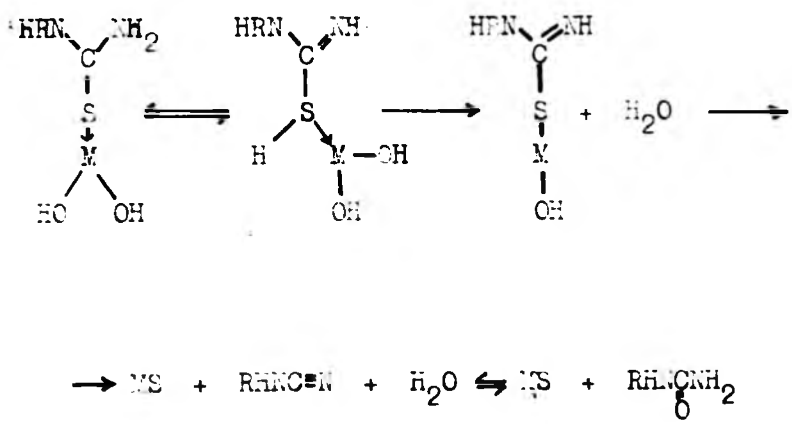


I

7iv With arsenic (III) chloride in acetone.

Reaction of thiourea with $AsCl_3$ in acetone results in the precipitation of a white solid (V) - $[AsCl_3(tu)_3]$. I.r. data indicates sulphur donation, the B ($1428cm^{-1}$) and C ($1425cm^{-1}$) bands shifting to higher energy and the F ($718cm^{-1}$) and G ($575cm^{-1}$) bands to lower frequency. The D band ($1080cm^{-1}$) shows very little change in position, but it is much weaker than that in free thiourea. The low i.r. region contains several absorptions, mixing of the ν(As-Cl) and ν(As-S) debars formal assignment of these bands. (N-C-N) and (N-C-S) deformation modes may also occur in this region.

The ^{1}H.N.M.R. spectrum of a fresh d^6DMSO solution of the complex exhibits one broad peak (9.84 δppm) dramatically shifted down field from thiourea (7.14 δppm). Decomposition of the solution occurs on standing, giving crystals of sulphur. Desulphurization of thiourea, by lead and mercury hydroxides, has been noted previously and was thought to occur after coordination via the sulphur atom:-[479,480]



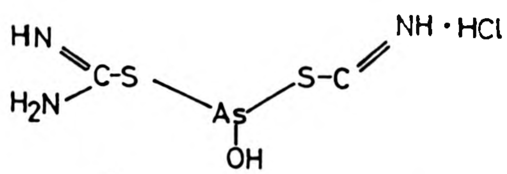
Similarly on reaction with $AsCl_3$ in water:-[481]

$$AsCl_3 + (H_2N)_2CS \xrightarrow{H_2O} [AsCl(CSN_2H_3)_2(H_2O)] + 2HCl$$

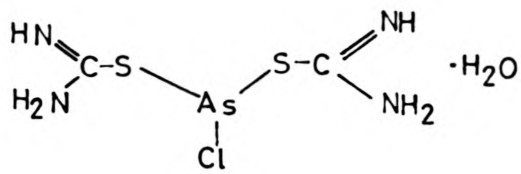
$$2\,[AsCl(CSN_2H_3)_2(H_2O)] \longrightarrow (NH_2)_2CS + 3(NH_2)_2CO + As_2S_3$$

Here adduct formation was observed prior to decomposition via obvious solvolysis. The complex $[AsCl(CSN_2H_3)_2.H_2O]$ was formulated as either (J) or (K).

The reaction of diphenyl thiourea with AsX_3 (X=Br,I) was reported to give 1:1 adducts as white and yellow solids respectively, only analytical data was presented.[482]



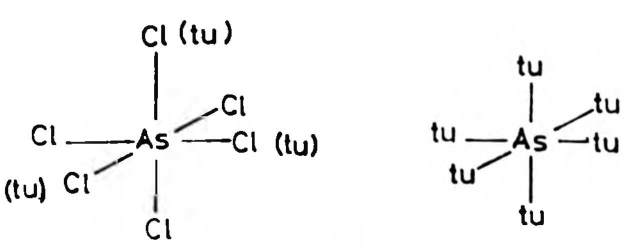
J



K

Ionic adducts of the type $[Me_2As(tu)]^+Cl^-$ and $[\{(Me_2As(tu)\}^+Cl^-(tu)]$ have been prepared, the latter was shown to contain thiourea coordinated via the sulphur atom, while the chlorine is present as the chloride ion [483] (Fig 7.3). Thiourea is also coordinated via sulphur in the complex trichloro [1,3 dimethyl 2(3H) imidazolethione] arsenic (III). Here two molecules are loosely joined into dimeric units via long As-Cl bridging bonds [484] (Fig 7.4). Similar structures were proposed for the analogous 1,1,3,3, tetramethyl 2-thiourea complexes of AsX_3 and $ArAsX_2$ (X=Cl,Br)[485].

Our complex, $[AsCl_3(tu)_3]$, is seen as an ionic structure (L), similar to its bismuth analogue.



L

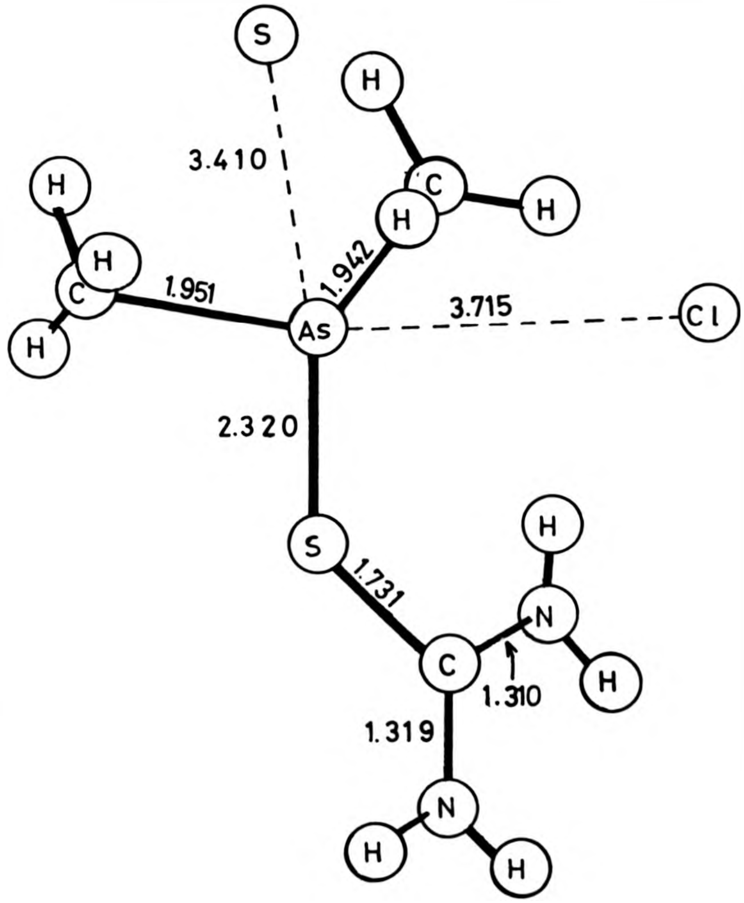


Fig. 7.3. Structural features of the cationic portion of $[(CH_3)_2As(tu)]^+.Cl^-.tu$.

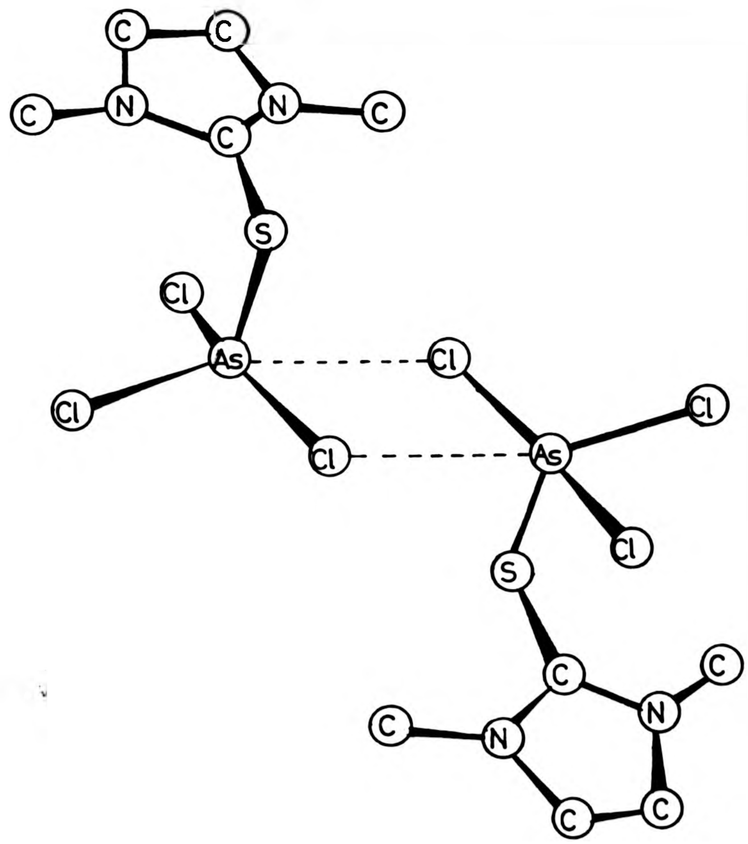
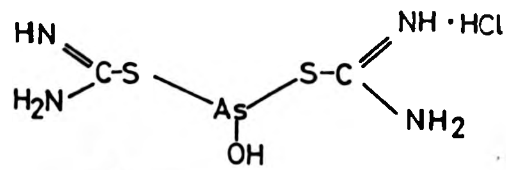
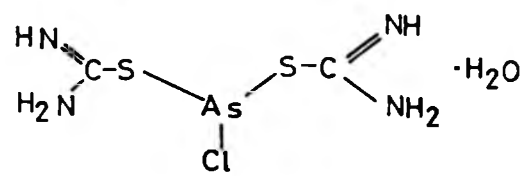


Fig. 7.4. Structure of the dimeric unit in $AsCl_3$(dmit)



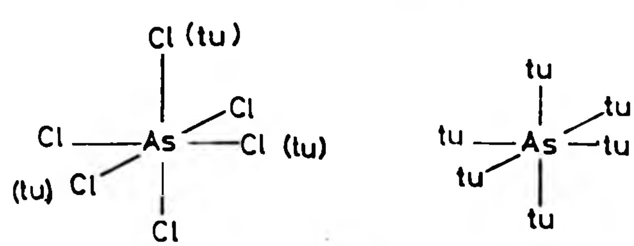
J



K

Ionic adducts of the type $[Me_2As(tu)]^+Cl^-$ and $[\{(Me_2As(tu)\}^+Cl^-(tu)]$ have been prepared, the latter was shown to contain thiourea coordinated via the sulphur atom, while the chlorine is present as the chloride ion [483] (Fig 7.3). Thiourea is also coordinated via sulphur in the complex trichloro [1,3 dimethyl 2(3H) imidazolethione] arsenic (III). Here two molecules are loosely joined into dimeric units via long As-Cl bridging bonds [484] (Fig 7.4). Similar structures were proposed for the analogous 1,1,3,3, tetramethyl 2-thiourea complexes of AsX_3 and $ArAsX_2$ (X=Cl,Br)[485].

Our complex, $[AsCl_3(tu)_3]$, is seen as an ionic structure (L), similar to its bismuth analogue.

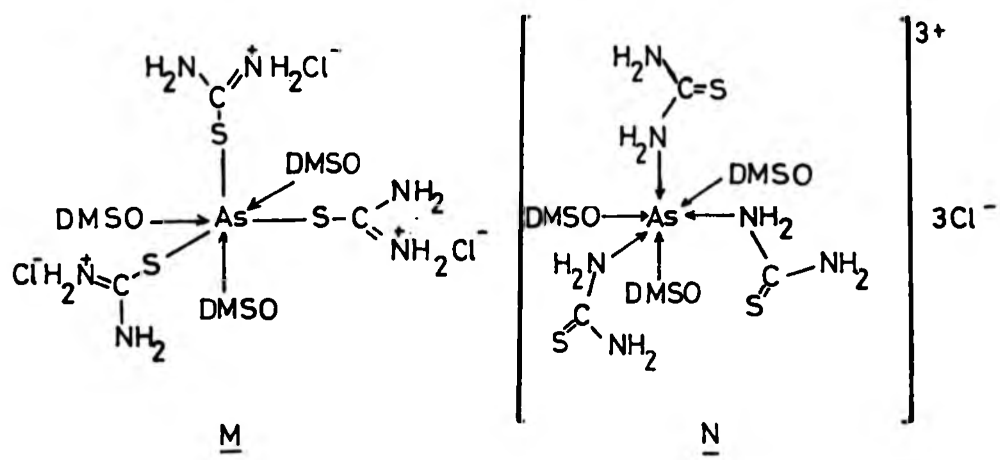


L

7v With arsenic (III) chloride in dimethylsulphoxide.

Carrying out the reactions of $AsCl_3$ with thiourea in DMSO rather than acetone leads to the isolation of a second product (IV), containing both coordinated thiourea and DMSO. ^{1}H.N.M.R. data (9.76,6.05 δppm) for the complex in d^6DMSO indicates the presence of two types of NH protons associated with thiourea. Coordinated DMSO is confirmed by a ^{1}H.N.M.R. spectrum of the complex dissolved in D_2O.

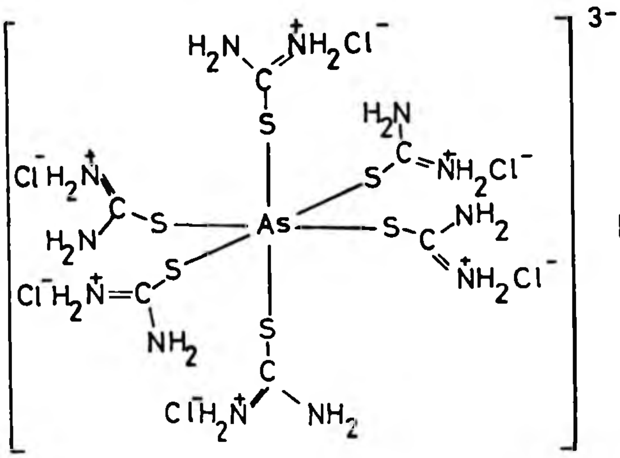
The presence of two types of NH protons suggest two possible types of structures (M) or (N).



However (N) is ruled out on the basis of i.r. data. The B (1480cm^{-1}) and C (1422cm^{-1}) bands exhibit high frequency shifts and the F (705cm^{-1}) and G (610cm^{-1}) bands low energy shifts commensurate with sulphur donation. Further the weakening of the D (1081cm^{-1}) band rather than a strengthening and the lack of a significant negative shift in the frequency of the ν(NH) modes rules out nitrogen coordination (Table7.3).

In the i.r. spectrum of DMSO the band at 1045 cm^{-1} represents almost equal contributions from two molecular motions, ν(S-O) and CH_3 rocking.[484] The direction of the frequency shift of this band upon complexation can be used to distinguish between oxygen and sulphur bound DMSO. A decrease in frequency accompanies oxygen coordination whereas sulphur donation leads to a frequency increase.[485] For $[AsCl_3(tu)_3(DMSO)_3]$ a band is located at 1015 cm^{-1}, indicating oxygen donation. For comparison $[SbCl_3(DMSO)_2]$ absorbs at 1028 cm^{-1}.

The ^{13}C.N.M.R. spectrum of D_2O solution of the product contains two singlets, one at 39.71 δppm is assigned to $^{13}\underline{C}H_3$-S and the other at 167.23 δppm to $(NH_2)_2{}^{13}\underline{C}S$. This and ^{1}H.N.M.R. evidence indicates that the thiourea is not dissociated in solution. Structures such as (M) and (P) are envisaged.



$[As(DMSO)_6]^{3+}$

P

7vi With phosphorus (III) chloride

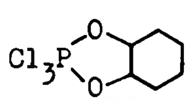
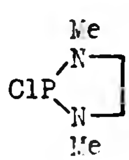
There are innumerable instances of phosphorus (III) compounds acting as donors to a wide variety of metal centres.[431] Acceptor properties will be only slight and this is reflected by the lack of data for such systems. Trost[486] claimed to have prepared 1:1 adducts of Et_3N with ECl_3 and ECl_5(E=P,As,Sb and Bi). No physical data was offered and the results could not be substantiated for phosphorus and antimony by Holmes and Bertaut.[487-490] A weak complex was found between Me_3N and PCl_3 at low temperatures but dissociated on warming to 273K. More recently this complex has been subject to a Raman spectral study.[432]

Reaction of PCl_3 with thiourea in a mixture of DMF and benzene as solvent, gave a white solid (VII) which analysed for $[PCl_3(tu)(DMF)_2]$. ^{1}H.N.M.R. spectral evidence supports this formulation, resonances being observed at 3.269 (3), 3.367(3) and 8.674(1) δ ppm due to DMF and at 7.657(2) δ ppm due to thiourea. The thiourea protons are shifted by ~0.6 ppm downfield from that of free thiourea suggesting that the complex does not dissociate in solution. A singlet (2.180 δ ppm) in the ^{31}P.N.M.R. spectrum of the complex is shifted dramatically upfield from that of PCl_3, and indicates a unique phosphorus environment. This rules out any ionic formulations such as $[PCl_2tu_2(DMF)_2]^+[PCl_4]^-.2DMF$. Tricoordinate P(III) compounds bearing at least one electronegative substituent generally give ^{31}P chemical shifts of $<-100\,\delta$ ppm, positive shift values usually being indicative of phosphines of the type PR_3 (R= alkyl, aryl or H). Five and six coordinate phosphorus compounds generally have positive

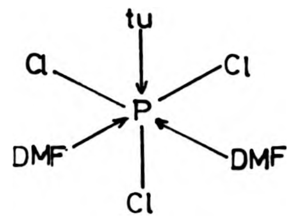
^{31}P chemical shifts, while phosphonium salts and phosphorus ylids fall into the range -30 to -5δppm (Table 7.4).[177,491] The value of 2.180 δppm for our complex seems indicative of a five or six coordinate species. The two singlets in the ^{13}C.N.M.R. spectrum are assigned to thiourea (155.930 δppm) and DMF (153.733 δppm). The former is shifted upfield by ~30 δppm from free thiourea, supporting the ^{1}H.N.M.R. evidence, that the complex is not dissociated in solution.

In the infra-red spectrum (Table 7.3) the low energy shifts of the composite B (1460cm^{-1}) and C (1410cm^{-1}) bands and the intense (NH) stretching vibrations (3260,3200,3100cm^{-1}) are indicative of nitrogen coordination. However sulphur coordination is indicated by the low energy shifts of the G (610cm^{-1}) and F (713cm^{-1}) bands. Assignments for this 600 -800cm^{-1} region are complicated by DMF vibrations also occurring in this region. The (O-C-N) bending mode occurs at 657cm^{-1} in free DMF, the corresponding vibration is tentatively located at 652cm^{-1} in the complex. A high energy shift is usually expected in complexes of DMF bound via the oxygen atom,[492] for comparison the band is located at 670 and 675 cm^{-1} in the complexes $[Sb(DMF)_6{}^{3+}].3(ClO_4)^-$ and $[As(DMF)_5]^{3+}.3(ClO_4)^-$ respectively.[478] Further the carbonyl stretching mode is located at 1676cm^{-1} in the complex compared to 1675cm^{-1} in free DMF, suggesting only very weak coordination if any, between the phosphorus and the oxygen atom of DMF. It should be noted that the bending (NH) mode of thiourea is also found in this region. Bands at 550 and 435 cm^{-1} are assigned to ν(P-Cl) modes.

Table 7.4 ^{31}P.N.M.R. data for selected phosphorus compounds.

Compound	^{31}P chemical shift (δ ppm; ref H_3PO_4)
PCl_3	-219
$MePCl_2$	-191
Me_2PCl	-94
Me_3P	+62
PH_3	+240
PCl_5	+80
PPh_5	+89
$(Me_4P)^+Br^-$	-25
$(NPCl_2)_3$	-20
$(NPCl_2)_4$	+7
$(NPCl_2)_5$	+17
PCl_4^+	-96
PCl_6^-	+281
	+26
$S{=}PCl(NMe_2)_2$	-91
$ClP(NMe_2)_2$	-159
	-167
$OPCl_3$	-2
$SPCl_3$	-30

In view of the limited evidence for Lewis acid behaviour of PCl_3, it seems extremely unlikely that the complex is a simple six-coordinate donor-acceptor complex (Q).

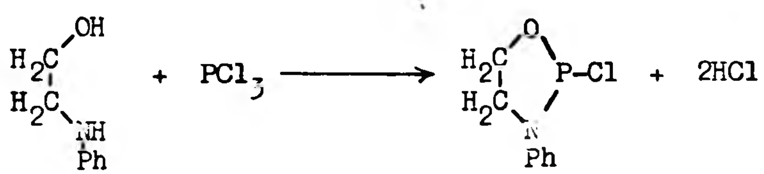


Q

Phosphorus (III) halides are known to react with a variety of primary and secondary amines, eliminating HCl to form P-N bonds:- [177,493]

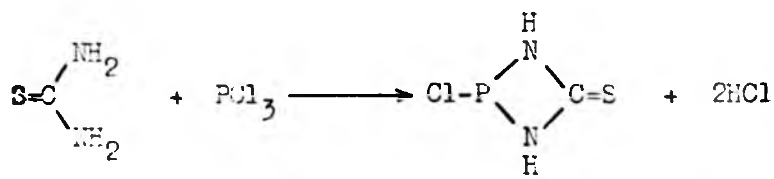
$$2R_2NH + PCl_3 \longrightarrow R_2NPCl + R_2NH_2^+Cl^-$$

$$3Bu^tNH_2 + PCl_3 \longrightarrow \tfrac{1}{2}(Bu^t\,PNCl)_2 + 2\,Bu^tNH_3^+Cl^-$$



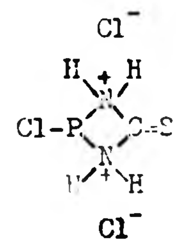
These reactions generally rely on removal of HCl to help the reaction proceed, usually by addition of excess base. Thiourea contains two amine centres capable of reaction with PCl_3;

eg.



[1]^{1}H.N.M.R. and analytical data precludes such a product unless present as the hydrochloride (R), with DMF present either

weakly coordinated or as solvent of crystallisation.



R

APPENDIX A.

EXPERIMENTAL TECHNIQUES.

Due to the extreme air/moisture sensitivity of the majority of materials described in this thesis, a number of specialised preparative and manipulative techniques were employed. These involved the handling of the materials either under an inert atmosphere or in a high vacuum.

Glassware was soaked in chromic acid and dried by baking in an oven at 398K for several hours prior to use. Where possible apparatus was flamed out whilst being pumped on the vacuum line.

The 'Dry Box. A steel glove box with a Perspex front and an 'air' lock type entrance port, was used to maintain a dry, oxygen-free, nitrogen atmosphere for the handling of the materials. Phosphorus pentoxide in open dishes removed residual traces of moisture.

The Vacuum Line. A standard, all glass, high vacuum system (Fig. A.1), the vacuum was produced and maintained by a Genevac double stage rotary piston vacuum pump, type GHD3. An electrically heated mercury diffusion pump, was also used.

Solvents were rigorously dried prior to use in solvent stills (Fig.A.2) which readily allowed a rapid reflux, collection and removal of solvents under a dry nitrogen atmosphere. Chloroform was distilled from phosphorus pentoxide, the other common solvents from calcium hydride. Diethylether was dried by standing over sodium wire and tetrahydrofuran distilled at reduced pressure from sodium/benzoquinone.

The majority of reactions were carried out in single

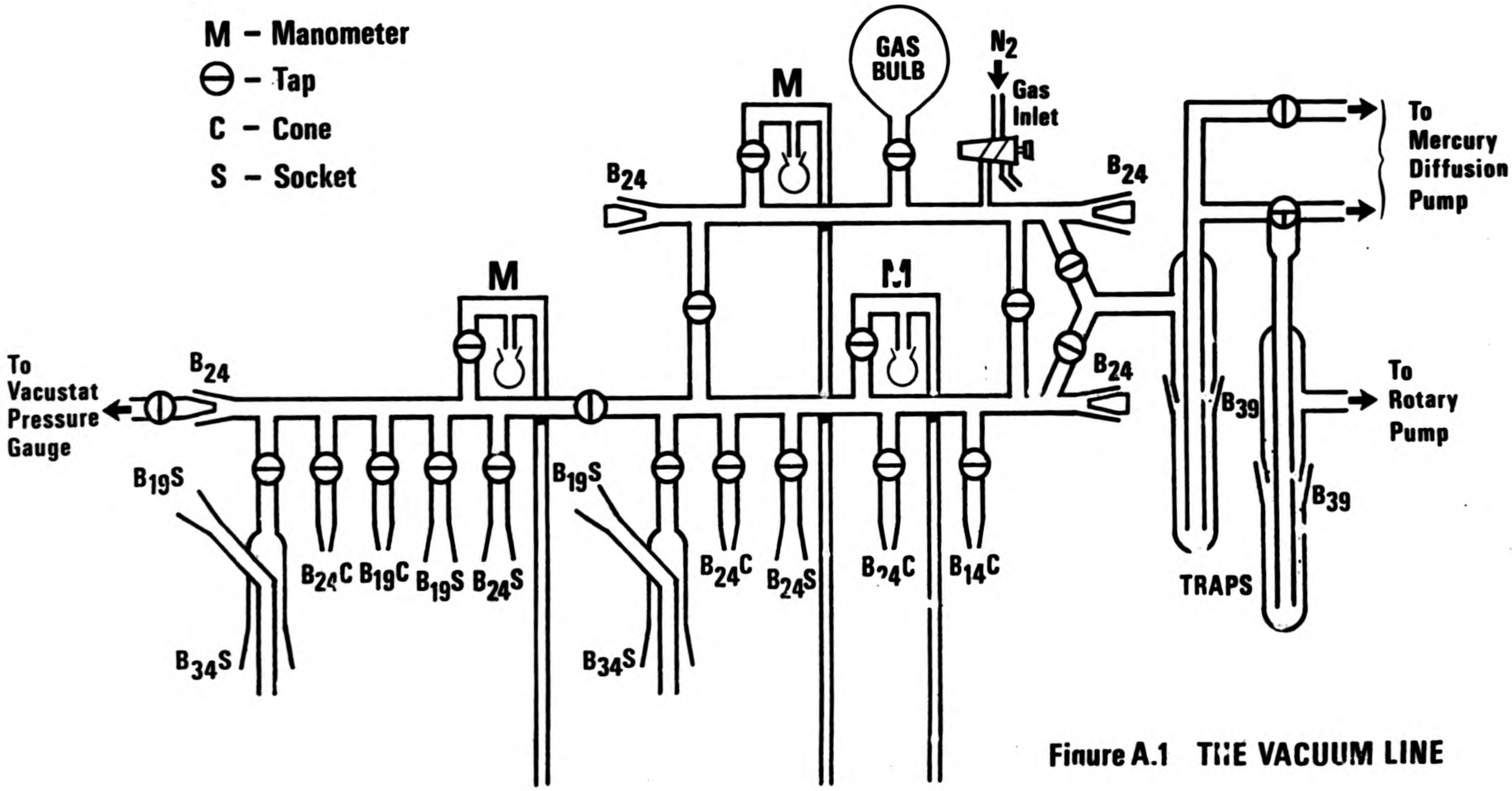


Figure A.1 THE VACUUM LINE

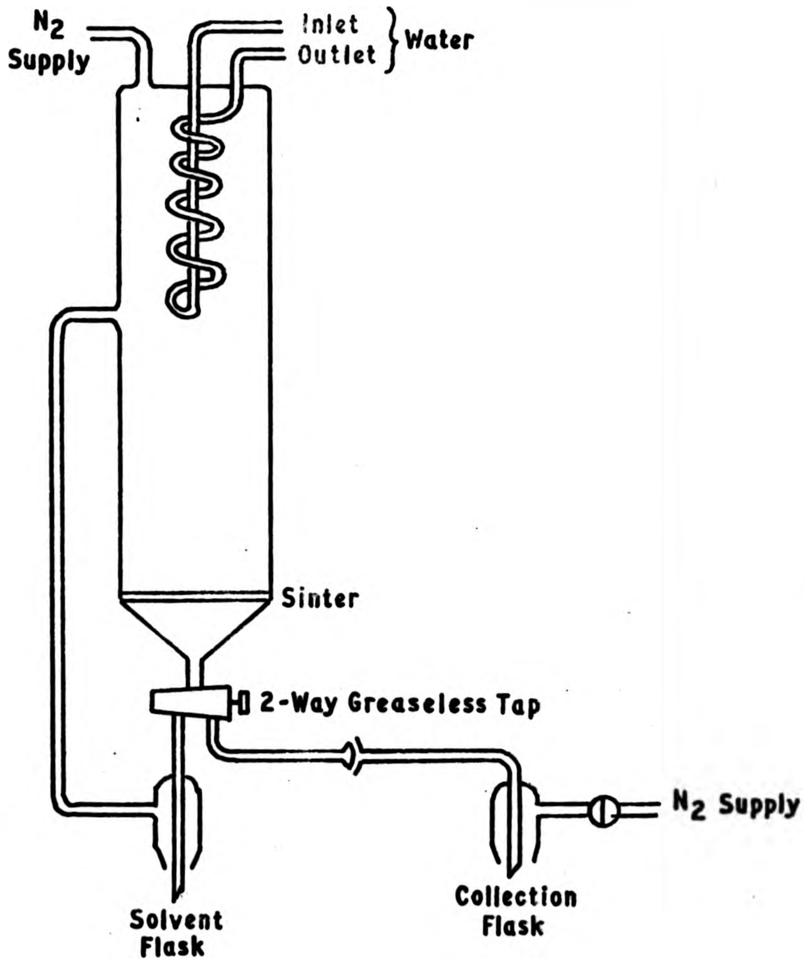


FIGURE A.2. SOLVENT STILL

ampoules (Fig. A.3) which could be sealed via the teflon screw tap (A). Double ampoules (Fig. A.4) were used for those cases where the product of the reaction was soluble, but the starting material insoluble. In particular for the preparation of trimethylamine adducts of the early transition metal halides. This type of reaction vessel allowed the isolation of the product in flask C while the insoluble starting material remains in flask A.

The main preparative procedures used are given below.

Reaction of solid + solid. The two solid reactants were loaded into a single ampoule. Dry degassed solvent was distilled onto the solids by use of the vacuum line.

Reaction of solid + volatile liquid. The solid was loaded into a single ampoule. The volatile liquid, and any solvent required, was then distilled onto the solid under reduced pressure on the vacuum line.

Reaction of solid + involatile liquid or soluble solid. The solid reactant was loaded into a single ampoule and the involatile liquid or soluble solid into a flask. By use of the vacuum line as in Fig. A.5, solvent could be distilled into the flask A and the solution transferred to the ampoule.

Extraction of products. If either the product or reactant was insoluble but the other component soluble, purification could be achieved by an extraction process (Fig. A.6).

Column chromatography. Florisil and alumina, dried by baking in an oven at 398K and carboxymethyl cellulose (Whatmans CMII), dried by pumping in vacuo, were used as column packing materials.

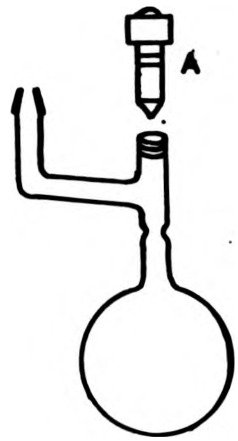


FIGURE A3. SINGLE AMPOULE

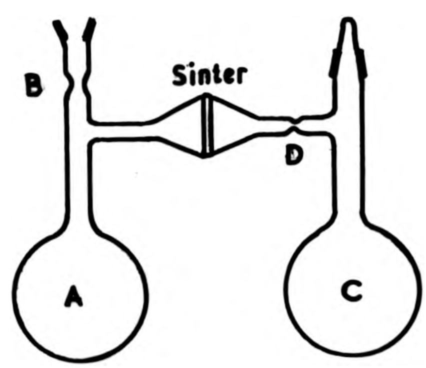


FIGURE A4. DOUBLE AMPOULE

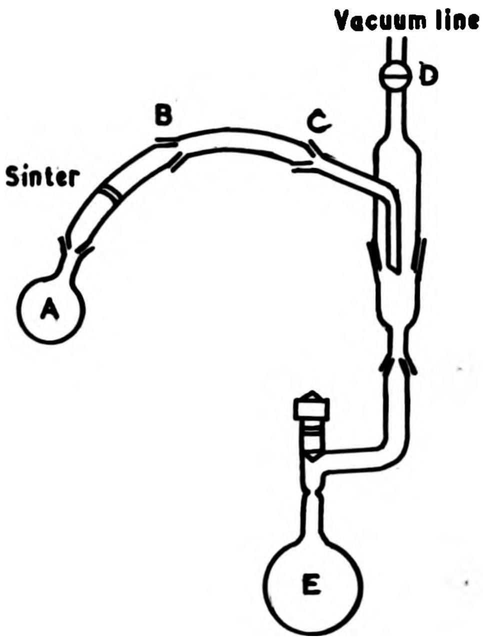


FIGURE A 5. LOADING ON EXTRACTION SYSTEM

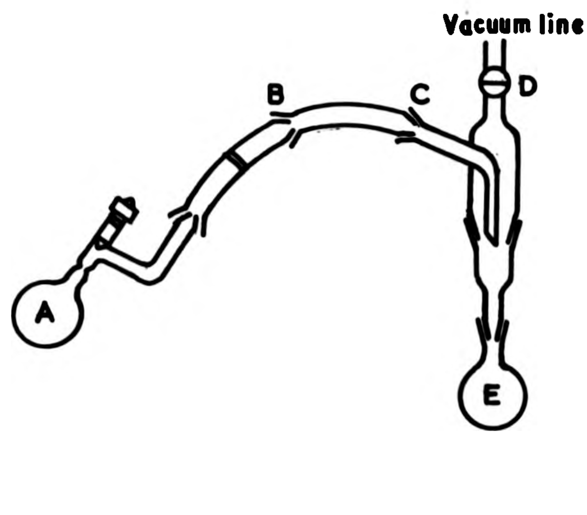


FIGURE A 6. EXTRACTION ON THE VACUUM LINE

Spectral measurements were recorded on the following instruments:

Infra-red spectra (4000-200cm^{-1}). Perkin-Elmer 621 grating infra-red spectrophotometer. Samples were run as nujol and hexachloro-butadiene mulls held between caesium iodide plates, or as solutions in caesium iodide windowed infra-red solution cells.

Far Infra-red spectra (400-50cm^{-1}). Research and Industrial Instruments F.S-720 Fourier spectrophotometer. The machine was calibrated against the rotational spectrum of water vapour. Samples were run as nujol mulls held between polythene plates.

Electronic spectra (700-180nm). Cary 14 spectrophotometer. Solution spectra were recorded in sealed 1 cm silica cells (Fig.A.7). The cell, containing the sample solution, was sealed under vacuum at the constriction B, allowing ready dilution of the solution to be made in situ.

Nuclear Magnetic Resonance spectra. High resolution ^{1}H, ^{13}C, ^{31}P- Bruker WH90 (90MHz) instrument, ^{1}H - Perkin-Elmer R12 (60MHz) spectrometer. ^{1}H and ^{13}C.N.M.R. spectra were calibrated against tetramethysilane, ^{31}P.N.M.R. spectra against 80% phosphoric acid in water. Sample solutions were sealed in pyrex N.M.R. tubes (Fig.A.8) under vacuum.

Mass spectra. VG Micromass 12 instrument.

Chemical Analysis. Butterworths Micro Analytical Centre, Teddington, Middlesex.

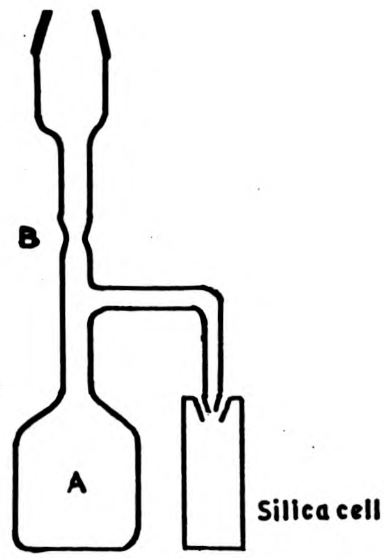


FIGURE A 7. U.V. CELL

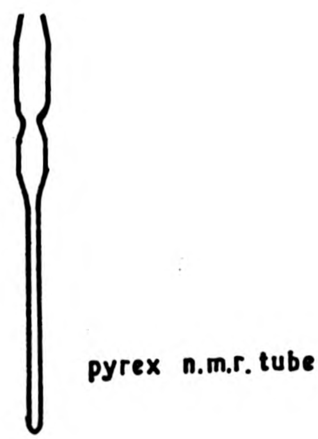


FIGURE A 8. N.M.R. TUBE

PURIFICATION AND PREPARATION OF STARTING MATERIALS.

Antimony (III) chloride. (May and Baker Ltd., Dagenham, Essex.) Colourless solid, mpt 346K, purified by sublimation in vacuo before use.

Arsenic (III) chloride. (Hopkin and Williams, Chadwell Heath, Essex). Colourless liquid, bpt 403K, used without further purification.

Bismuth (III) chloride. (Fisons, Loughborough, Leicestershire) White crystalline solid, mpt 503K, sublimed in vacuo prior to use.

Bis(cyclopentadienyl) bis (ethanethiolato)-titanium(IV). Prepared from $(C_5H_5)_2TiCl_2$ and EtSH using the method of Kopf and Schmidt,[494] as dark maroon-purple, malodourous crystals. The material was stored in sealed glass ampoules under nitrogen as very slow decomposition was observed in air.

Bis (cyclopentadienyl) titanium (IV) chloride. (Aldrich, Gillingham, Dorset.) Red crystals, mpt 563K, used as supplied.

Butylamine. (B.D.H.Ltd, Poole, Dorset) Liquid bpt 317K, used as supplied.

Chromium (III) chloride - Anhydrous. (Pfaltz and Bauer, Flushing, N.Y.) Purple platelets used without further purification.

Chromium (III) chloride tris (tetrahydrofuran). Prepared by literature method [290] as either a purple THF solution or by removal of solvent as a purple solid.

Deutero-benzene. (Fluorochem Ltd., Glossop, Dertyshire.) Dried with $LiAlH_4$ prior to use as an N.M.R. solvent.

Deutero-chloroform (Merck, Sharp and Dohme, 61 Darmstadt, Germany). Dried over P_2O_5 before use.

Deutero-dimethylsulphoxide. (Merck, Sharp and Dohme, 61 Darmstadt, Germany). Used as obtained.

Deuterated-water (Merck, Sharp and Dohme, 61 Darmstadt, Germany). Used as obtained.

Dicobalt octacarbonyl. (Strem Chemicals Inc., Danvers, Mass.). Stored at 273K in the dark and purified prior to use by vacuum sublimation.

Diiron enneacarbonyl. (Cambrian Chemicals, Croydon, Surrey). Stored at 273K in the dark, used as supplied.

Dimanganese decacarbonyl. (Strem Chemicals Inc., Danvers, Mass.). Stored in the dark at 273K, and purified before use by vacuum sublimation.

Dimethylamine. (B.D.H. Ltd, Poole Dorset.) Liquid bpt 280K, distilled from over KOH pellets prior to use.

Dimethylformamide. (B.D.H. Ltd, Poole, Dorset.). Colourless liquid, bpt 422-429K used as supplied.

Dimethylsulphoxide. (B.D.H. Ltd, Poole, Dorset.) Clear, colourless liquid, mpt 291K, decomposes on heating, used without further purification.

Dimethyltin (IV) chloride. Prepared by disproportionation of $SnCl_4$ and Me_4Sn[495]. White crystals, mpt 363K, purified by vacuum sublimation.

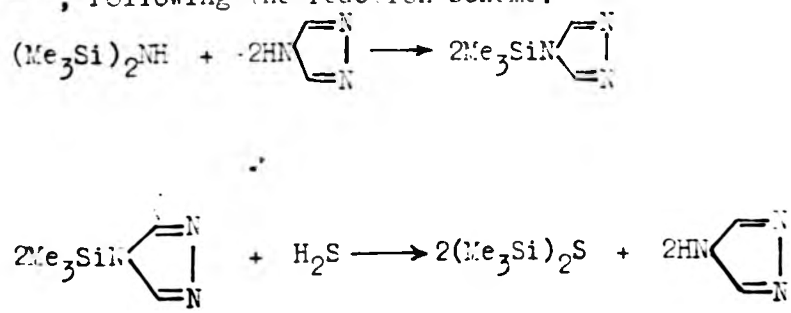
Dirhodium (I) tetracarbonyldichloride. Prepared by the method of McCleverty and Wilkinson,[496] from $[RhCl_3(H_2O)_3]$ and carbon monoxide gas. The orange solid was purified by vacuum sublimation.

<u>1,3 Di(tert-butyl)2,4 dichloro 1,3,2,4 diazadiphosphetidine</u>. Prepared according to the method of Jefferson et al,[150] from PCl_3 and Bu^tNH_2. White solid, mpt 317-319K, bpt at 0.5mmHg, 383K, purified by vacuum distillation.

<u>Hexachlorobutadiene</u>. (B.D.H.Ltd, Poole, Dorset). Spectroscopic grade used as supplied.

<u>Hexamethyldisiloxane</u>. Prepared following the hydrolysis of Me_3SiCl.[497] The colourless liquid product bpt 373K, was purified by fractional distillation from over P_2O_5.

<u>Hexamethyldisilathiane</u>. Prepared by the method of Armitage et al [498], following the reaction scheme:-



<u>EXTREME CARE</u> is required in handling hexamethyldisilathiane as it is particularly malodourous. All apparatus was soaked in $KMnO_3$ solutions after use to remove the odour and when handled in the dry box the outlet bubblers were supplemented with traps containing $KMnO_3$solution.

<u>Lithium n-butyl</u>. (Aldrich, Gillingham, Dorset). Supplied as an n-hexane solution.

<u>Lithium methyl</u>. (Aldrich, Gillingham, Dorset) Supplied as an Et_2O solution.

<u>Molybdenum hexacarbonyl</u>. (B.D.H.Ltd, Poole, Dorset.) Stored in

the dark at 273K, sublimed in vacuo prior to use.

Norbornadienyl tetracarbonyl molybdenum. Prepared by the literature method,[499] and sublimed in vacuo prior to use.

Nujol. (Fisons, Loughborough, Leicestershire). Spectroscopic grade, used as supplied.

Phosphorus (III) chloride. (Fisons, Loughborough, Leicestershire). Colourless, fuming liquid, used as supplied.

Pyridine. (Fisons, Loughborough, Leicestershire). Colourless liquid, distilled under reduced pressure from over KOH pellets before use.

1,4,7,10 Tetrazadecane. (Union Carbide Ltd, Southampton, Hants.). Distilled from over KOH pellets at reduced pressure prior to use.

Tetramethylsilane. (Merck, Sharpe and Dohme, 61 Darmstadt, Germany). Stored at 273K, used without further purification.

Tetramethyl tin (IV). Prepared from $SnCl_4$ and MeMgBr, colourless liquid bpt 351K.

Thiourea. (May and Baker Ltd, Dagenham, Essex.) White crystals, mpt 455K, used as supplied.

CARE, cancer suspect agent.

Tin (IV) chloride. (Fisons, Loughborough, Leicestershire) Colourless liquid, bpt 387K, used without further purification.

Titanium (IV) chloride. (Fisons, Loughborough, Leicestershire) Pale yellow liquid, bpt 409K, used as supplied.

Titanium (III) chloride-Anhydrous. (K and K laboratories, Plainview, N.Y.) Dark violet crystals used without further purification.

Titanium (III) chloride tris (tetrahydrofuran). $TiCl_3$ was extracted with boiling THF via a soxhlet thimble. The resulting pale blue solution was used directly or the solvent removed to give pale turquoise crystals of $[TiCl_3(THF)_3]$.

Triethylamine. (B.D.H. Ltd. Poole, Dorset) Colourless liquid, bpt 362K, distilled over KOH pellets under reduced pressure as required.

Trimethyl chlorosilane. A generous gift from Dow Corning Ltd Midland, Michigan, is gratefully acknowledged. Colourless liquid, bpt 332K, used as obtained.

Tris(2-Aminoethyl) amine. (Strem Chemicals Inc., Danvers, Mass.) Purified by fractional distillation at reduced pressure over KOH pellets.

Tris(2-dimethylamino)amine. (Strem Chemicals Inc., Danvers, Mass. Purified by fractional distillation over KOH pellets under reduced pressure prior to use.

Vanadium (III) chloride - Anhydrous. (K and K Laboratories, Plainview, N.Y.) Pink crystals used as supplied.

Vanadium (III) chloride tris(tetrahydrofuran). Prepared by extraction of VCl_3 with boiling THF via a soxhlet thimble. The solution could be used directly or mauve crystals of $[VCl_3(THF)_3]$ obtained by removal of solvent.

Zirconium metal. (Cerac/Pure Inc, Menomonee Falls, Wisconsin.) Used as obtained.

Zirconium (IV) chloride. Prepared from zirconium metal and chlorine gas in the apparatus shown in Fig.A.9. A slow stream of chlorine mixed with nitrogen carrier gas, was passed over the surface of the zirconium metal at 800K. The zirconium (IV) chloride sublimes out of the furnace into the receiver.

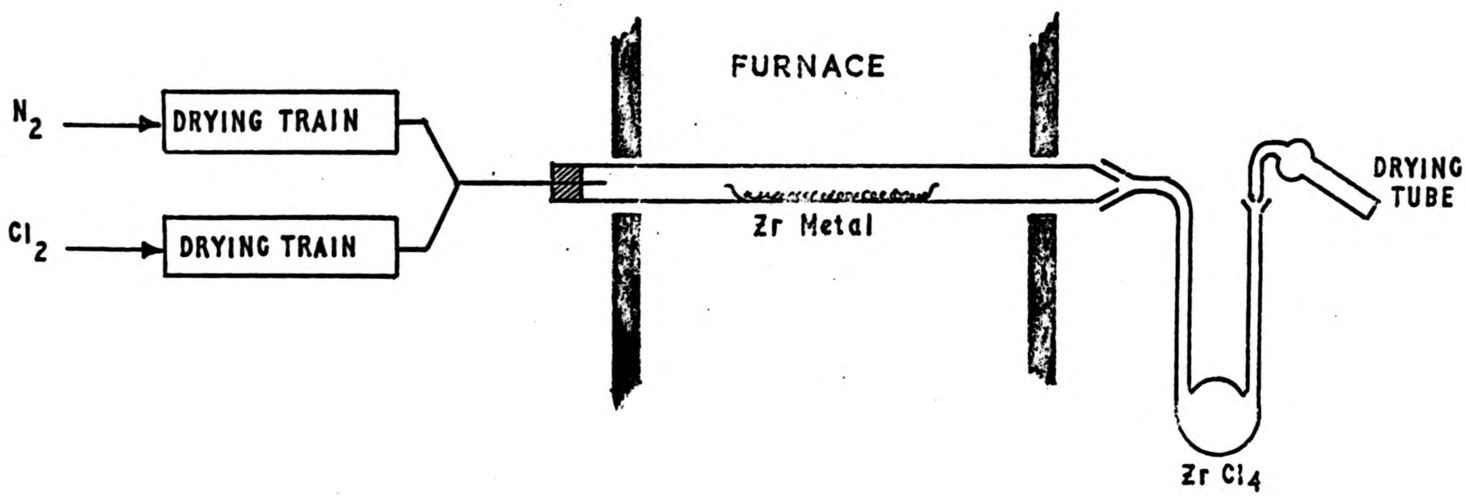


FIGURE A9. APPARATUS FOR THE PREPARATION OF Zr Cl_4

APPENDIX B.

INORGANIC NOMENCLATURE.

The contents of this appendix consist of short excerpts from the relevant sections of the report of the commission on the nomenclature of inorganic chemistry (1957)[500]. These give a brief outline of the general principles of inorganic nomenclature used in this thesis.

In general terms a coordination entity refers to molecules or ions in which there is an atom (A) to which are attached other atoms (B) or groups (C). The atom A is known as the nuclear or central atom, and all other atoms which are directly attached to A are known as coordinating or ligating atoms. Each central atom A has a characteristic coordination number or ligancy which is the number of atoms directly attached to it. The atoms B and groups C are called ligands. A group which contains more than one potential coordinating atom is referred to as a multidentate ligand. A chelate ligand is one attached to one central atom through two or more coordinating atoms, a bridging group is one attached to more than one centre of coordination. The whole assembly, with one or more central atoms and their ligands, is referred to as coordination entity, or more generally a coordination compound or complex.

The simple multiplying affixes, mono, di, tri, tetra, penta, hexa, octa, ennea (nona), deca, undeca, dodeca, etc, are used to indicate stiochiometric proportions, the extent of substitution and the number of identical coordinated groups. They are used by direct joining without hyphens. The multiplicative affixes bis, tris, tetrakis, pentakis, etc are used to avoid ambiguity. They are used by direct joining without hyphens but usually with enclosing marks around each whole expression to which the prefix applies.

Arabic numerals are used to designate the atoms at which there is a substituent or addition in a chain. Arabic numerals followed by + or - and enclosed in parentheses also are used to indicate the charge on a free or coordinated ion. Roman numerals are used in parentheses, after the name of the atom, to indicate the oxidation number of an element. The cipher 0 is used to indicate an oxidation state of zero, a negative oxidation state is indicated by the use of the negative sign with a Roman numeral.

The ligands are listed in alphabetical order regardless of their number, the name of a ligand being treated as a unit. Anionic ligands. In general, if the anion name ends in -ide, -ite, or -ate, the final 'e' is replaced by 'o', giving -ido, -ito, and -ato, respectively. Some exceptions are listed below:-

	Ion	Ligand.
F^-	fluoride	fluoro
Cl^-	chloride	chloro
Br^-	bromide	bromo
I^-	iodide	iodo
O^{2-}	oxide	oxo
H^-	hydride	hydrido
OH^-	hydroxide	hydroxo

O_2^{2-}	peroxide	peroxo
CN^-	cyanide	cyano

Neutral and Cationic ligands. The name of a coordinating molecule is used without change except for the special cases of water, which becomes aqua, and ammonia, which becomes ammine. Also the groups NO and CO, when linked directly to a metal atom become nitrosyl and carbonyl respectively. All neutral ligands, with the exception of those cited above are enclosed within brackets.

For geometrical isomers the prefixes cis, trans, fac and mer are used where they are sufficient to designate specefic isomers. Where locant designators are used they are lower case letters, the first ligand mentioned is given the lowest possible designator and the second ligand the next possible designators etc.

Bridging atoms or groups are indicated by adding the Greek letter μ immediately before its name and separating the name from the rest of the complex by hyphens. Two of more bridging groups of the same kind are indicated by a multiplicative prefix immediately prior to the $-\mu-$. The bridging groups are listed with the other groups in alphabetical order unless the symmetry of the molecule permits simpler names by the use of multiplicative prefixes. If the same ligand is present as a bridging ligand and as a non-bridging ligand, it is cited first as a bridging ligand.

Polynuclear compounds without bridging groups, containing metal-metal bonds, when symmetrical, are named by the use of multiplicative prefixes. When unsymmetrical one central atom shall be treated as ligand on the other centre.

For linkage isomerism the different points of attachment of a ligand maybe denoted by adding the italicized symbol(s) for the atom or atom through which attachment occurs at the end of the name of the ligand. In some cases different names are already in use for alternative modes of attachment, eg. thiocyanato (-SCN) and isothiocyanato (-NCS); nitro ($-NO_2$) and nitrito (-ONO).

Other prefixes used are listed below, they are italicized and separated from the rest of the name by hyphens.

Antiprismo- eight atoms bound into a rectangular antiprism.

asym- asymmetrical.

catena- a chain structure, often used to designate linear polymeric substances,

closo- a cage or slosed structure.

cyclo- a ring structure.

dodecahedro- eight atoms bound into a dodecahedron with triangular faces.

hexahedro- eight atoms bound into a hexahedron.

hexaprismo- twelve atoms bound into a hexagonal prism

icosahedro- twelve atoms bound into a triangular icosahedron.

nido- a nest like structure.

octahedro- six atoms bound into an octahedron.

pentaprismo- ten atoms bound into a pentagonal prism.

quadro- four atoms bound into a quadrangle.

sym- symmetrical.

tetrahedro- four atoms bound into a tetrahedron.

triangulo- three atoms bound into a triangle.

triprismo- six atoms bound into a triangular prism.

σ- signifies that one atom of the group is attached to a metal.

BIBLIOGRAPHY.

BIBLIOGRAPHY.

REFERENCES.

1. R. Colton and J. H. Canterford. "Halides of the first-row transition metals." Wiley (1969)

2. B. Krebs. Angew. Chem. Internat. Edn. 8 146 (1969)

3. J. W. Collier, A. R. Fox, I. G. Hinton and F. G. Mann. J. Chem. Soc. 1819 (1964)

4. A. Immirzi and A. Musco. Chem. Comm. 400 (1974)

5. M. Matsumoto, H. Yoshioka, K. Nakatsu, T. Yoshida and S. Otsuka. J. Amer. Chem. Soc. 96 3322 (1974)

6. D. C. Bradley and K. J. Fisher. J. Amer. Chem. Soc. 93 2058 (1971)

7. P. G. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek. Coordination Chem. Rev. 24 1 (1977)

8. D. C. Bradley, M. B. Hursthouse and P. F. Rodesiler. Chem. Comm. 14 (1969)

9. M. B. Hursthouse and P. F. Rodesiler. J. Chem. Soc. Dalton. 2100 (1972)

10. J. S. Ghotra, M. B. Hursthouse and A. J. Welch. Chem. Comm. 669 (1973)

11. A. J. Canty, A. Marker and B. M. Gatehouse. J. Organometallic Chem. 88 C31 (1975)

12. R. B. Roof, A. C. Larson and D. T. Cromer. Acta Cryst. B24 269 (1968)

13. G. G. Messmer and G. J. Palenik. Canad. J. Chem. 47 1440 (1969)

14. H. B. Gray. in "Transition metal chemistry."

Ed. R.L.Carlin. Edward Arnold. 1 239 (1965)

15. J.A.McCleverty. Progr. Inorg. Chem. 10 49 (1969)

16. J.D.Forrester, A.Zalkin and D.H.Templeton. Inorg. Chem. 3 1500 (1964)

17. R.G.Hayter and F.S.Humiec. J. Amer.Chem. Soc. 84 2004 (1962)

18. R.G.Hayter and F.S.Humiec. Inorg. Chem. 12 1701 (1965)

19. J.S.Wood. Progr. Inorg. Chem. 16 227 (1972)

20. B.F.Hoskins and F.D.Williams. Coordination Chem. Rev. 9 365 (1972-1973)

21. L.Sacconi. Coordination Chem. Rev. 8 351 (1972)

22. P.L.Orioli. Coordination Chem. Rev. 6 285 (1971)

23. M.Di Vaira and P.L.Orioli. Inorg. Chem. 6 955 (1967)

24. J.Donahue and A.Caron. Acta Cryst. 17 663 (1964)

25. R.D.Cramer, R.V.Lindsey, C.T.Prewitt and U.G.Stolberg. J. Amer. Chem. Soc. 87 658 (1965)

26. P.Dapporto and L.Sacconi. Chem. Comm. 1091 (1969)

27. L.Sacconi, P.L.Orioli and M.Di Vaira. J. Amer. Chem. Soc. 87 2059 (1965)

28. C.M.Harris and R.S.Nyholm. J. Chem. Soc. 4375 (1956)

29. B.F.Hoskins, R.L.Martin and A.H.White. Nature 211 627 (1966)

30. P.Pauling, G.B.Robertson and G.A.Rodley. Nature 207 73 (1965)

31. K.N.Raymond, P.W.Corfield and J.A.Ibers. Inorg. Chem. 7 1362 (1968)

32. R.Eisenberg and J.A.Ibers. J. Amer. Chem. Soc. 87 3776

(1965)

33. R.Eisenberg and J.A.Ibers. Inorg. Chem. 5 411 (1966)

34. R.A.D.Wentworth. Coordination Chem. Rev. 9 171 (1972-1973)

35. R.Eisenberg. Progr. Inorg. Chem. 12 295 (1970)

36. J.H.Parks, B.E.Wagner and R.H.Holm. J. Amer. Chem. Soc. 92 3500 (1970)

37. M.R.Churchill and A.H.Reis. Chem. Comm. 879 (1970)

38. M.R.Churchill and A.H.Reis. Chem.Comm. 1307 (1971)

39. E.L.Muetterties and C.M.Wright. Quart. Rev. 21 109 (1967)

40. M.G.B.Drew. Progr. Inorg. Chem. 23 67 (1977)

41. M.G.B.Drew, A.H.binOthman and S.M.Nelson. J. Chem. Soc. Dalton. 1394 (1976)

42. M.G.B.Drew. J.Chem. Soc. Dalton. 1329 (1972)

43. A.Zalkin, D.H.Templeton and D.G.Karraker. Inorg. Chem. 8 2680 (1969)

44. I.J.Bear and W.G.Mumme. Acta Cryst. B26 1140 (1970)

45. S.J.Lippard. Progr. Inorg. Chem. 21 91 (1976)

46. D.L.Lewis and S.J.Lippard. J. Amer. Chem. Soc. 97 2697 (1975)

47. R.V.Parish. Coordination Chem. Rev. 1 439 (1966)

48. S.J.Lippard. Progr. Inorg. Chem. 8 109 (1967)

49. M.G.B.Drew. Coordination Chem. Rev. 24 179 (1977)

50. D.L.Kepert. Progr. Inorg. Chem. 24 179 (1977)

51. G.Marangoni, S.Degetto, R.Graziani, G.Bombieri and E.Forsellini. J. Inorg. Nuclear Chem. 36 1787 (1974)

52. K.Bowman and Z.Dori. Chem. Comm. 636 (1968)

53. G.L.Glen, J.V.Silverton and J.L.Hoard. Inorg. Chem. 2 250 (1963)

54. J.V.Silverton and J.L.Hoard. Inorg. Chem. 2 243 (1963)

55. D.R.Sears and J.H.Burns. J. Chem. Phys. 41 3478 (1964)

56. J.Fischer, R.Elchinger and R.Weiss. Chem. Comm. 329 (1967)

57. S.C.Abrahams, A.P.Ginsberg and K.Knox. Inorg. Chem. 3 558 (1964)

58. G.E.Toogood and C.Chieh. Canad. J. Chem. 53 831 (1975)

59. S.Scavnicar and B.Prodic. Acta Cryst. 18 698 (1965)

60. P.S.Braterman. "Metal carbonyl spectra" Academic Press (1975)

61. P.S.Braterman. Structure and Bonding 26 1 (1976)

62. L.M.Haines and M.H.B.Stiddard. Adv. Inorg. Chem. Radiochem. 12 53 (1969)

63. T.A.Manuel. Adv. Organometallic Chem. 3 181 (1965)

64. E.W.Abel. Quart. Rev. 17 133 (1963)

65. K.Nakamoto. "Infra-red spectra of inorganic and coordination compounds." Wiley-Interscience. (1970)

66. D.M.Adams. "Metal-ligand and related vibrations." Edward Arnold. (1967)

67. W.D.Horrocks and R.C. Taylor. Inorg. Chem. 2 723 (1963)

68. A.Reckziegel and M.Bigorgne. J. Organometallic Chem. 3 341 (1965)

69. F.A.Cotton. Inorg. Chem. 3 702 (1964)

70. B.V.Lokshin, E.B.Rusach, Z.P.Valueva, A.G.Ginzburg and

.Kolobora. J. Organometallic Chem. 102 535 (1975)

71. J.C.Kotz and D.G.Pedrotty. J. Organometallic Chem. 22 425 (1970)

72. J.R.Ferraro. "Low frequency vibrations of inorganic and coordination compounds." Plenum Press. (1971)

73. D.W.James and M.J.Nolan. Progr. Inorg. Chem. 9 195 (1968)

74. A.Finch, P.N.Gates, K.Radcliffe, F.N.Dickson and F.F.Bentley. "Chemical applications of far infra-red spectroscopy." Academic Press. (1970)

75. F.F.Bentley, L.D.Smithson and A.L.Rozek. "Infra-red spectra and characteristic frequencies ~700-300cm^{-1}."
Interscience. (1968)

76. R.J.H.Clark. Spectrochim. Acta. 21 955 (1965)

77. R.J.H.Clark. in "Halogen chemistry." Vol. 3 Ed. V.Gutman. Academic Press. (1967)

78. A.Chakravorty. in "Spectroscopy in inorganic chemistry." Vol. 1 Eds. C.N.Rao and J.R.Ferraro. Academic Press. (1970)

79. R.K.Harris and B.E.Mann. "N.M.R. and the periodic table." Academic Press, (1978)

80. M.Grayson and E.J.Griffith (Eds.). "Topics in phosphorus chemistry." Vol. 5. Interscience. (1967)

81. J.W.Emsley, J.Feeney and L.Sutcliffe. "High resolution nuclear magnetic resonance spectroscopy." Pergamon (1965)

82. K.Vrieze and P.W.N.M.van Leeuwen. Progr. Inorg. Chem. 14 1 (1971)

83. L.M.Jackman and F.A.Cotton (Eds). "Dynamic nuclear magnetic resonance spectroscopy." Academic Press (1975)

84. A.Misono, Y.Uchida, M.Hidai and M.Araki. Chem. Comm. 1044 (1968)

85. R.R.Holmes and R.M.Deiters. J. Amer. Chem. Soc. 90 5021 (1968)

86. J.P.Jesson and P.Meakin. J. Amer. Chem. Soc. 95 1344 (1973)

87. C.A.Tolman, P.Z.Meakin, D.I.Lindner and J.P.Jesson. J. Amer. Chem. Soc. 96 2762 (1974)

88. J.G.Bullitt, F.A.Cotton and T.J.Marks. Inorg. Chem. 11 671 (1972)

89. O.A.Gansow, A.R.Burke and W.D.Vernon. J. Amer. Chem. Soc. 94 2550 (1972)

90. R.D.Adams and F.A.Cotton. J. Amer. Chem. Soc. 95 6589 (1973)

91. A.P.B.Lever. "Inorganic electronic spectroscopy." Elsevier. (1968)

92. C.J.Ballhausen. "Introduction to ligand field theory." McGraw-Hill. (1962)

93. L.E.Orgel. "An introduction to transition metal chemistry, ligand field theory." 2nd. Edition. Methuen and John Wiley. (1966)

94. Y.Tanabe and S.Sugano. J. Phys. Soc. Japan. 9 753 (1954)

95. D.Nicholls. "Complexes and first-row transition elements." Macmillan. (1974)

96. [illegible] "Spectroscopy in inorganic chemistry." Vol. 1 Eds. C.N.R.Rao and J.R.Ferraro. Academic Press. (1970)

97. [illegible] Adv. Organometallic Chem. 6 273 (1968)

98. [illegible].Chambers, F.Glocking and J.R.C.Light. Quart. Rev.

22 317 (1968)

99. J.Lewis and B.F.G.Johnson. Accounts Chem. Res. 1 245 (1968)

100. B.F.G.Johnson, R.D.Johnston, J.Lewis and B.H.Robinson. J. Organometallic Chem. 10 105 (1967)

101. R.J.H.Clark and R.E.Hester. (Eds). "Advances in infra-red and raman spectroscopy." Heyden (1975)

102. P.B.Ayscough. "Electron spin resonance in chemistry." Methuen. (1967)

103. V.I.Goldanskii and R.H.Herber. "Chemical applications of mossbauer spectroscopy." Academic Press. (1968)

104. R.S.Drago. "Physical methods in inorganic chemistry." Van Nostrand Reinhold Co. (1965)

105. L.Pauling. "The nature of the chemical bond." 3rd edition. Cornell University Press. (1960)

106. C.J.Ballhausen and H.B.Gray. "Molecular orbital theory." Benjamin. (1964)

107. For general review see I.Haiduc. "The chemistry of inorganic ring systems." Wiley. (1970)

108. I.U.P.A.C. "Nomenclature of organic chemistry, sections A,B,and C." 2nd edition. Butterworths. (1971)

109. D.B.Sowerby. in "M.T.P. International review of science." Ed. H.J.Emeleus. Butterworths. 2 117 (1972)

110. R.Keat and R.A.Shaw. in "Organic phosphorus compounds." Eds. G.M.Kosolapoff and L.Maier. Wiley-Interscience. Vol 6 (1973)

111. S.S.Krishnamurthy, A.C.Sau and M.Woods. Adv. Inorg. Chem. Radiochem. 21 41 (1978)

112. H.R.Allcock. Chem. Rev. 72 315 (1972)

113. For a review see D.E.C.Corbridge. "Topics in phosphorus chemistry." 3 57 (1966)

114. C.E.Brion, D.J.Oldfield and N.L.Paddock. Chem. Comm. 226 (1966)

115. D.P.Craig. Chem. Ind. (London) 3 (1958)

116. M.J.S.Dewar, E.A.C.Lucken and M.A.Whitehead. J. Chem. Soc. 2423 (1960)

117. M.A.Whitehead. Canad. J. Chem. 42 1212 (1964)

118. M.G.Acock, R.A.Shaw and F.B.G.Wells. J. Chem. Soc. 121 (1964)

119. E.Fluck, Becke-Goehring and Loppel. Z. anorg. Chem. 322 239 (1963)

120. C.T.Ford, F.E.Dickson and I.I.Bezman. Inorg. Chem. 3 177 (1964)

121. B.Grushkin, M.G.Sanchez and R.G.Rice. Inorg. Chem. 3 623 (1964)

122. F.S.Humiec and I.I.Bezman. J. Amer. Chem. Soc. 83 .210 (1961)

123. R.A.Shaw and C.Stratton. J. Chem. Soc. 5004 (1962)

124. B.W.Fitzsimmons and R.A.Shaw. Inorg. Synth. 8 77 (1966)

125. A.P.Carroll and R.A.Shaw. J. Chem. Soc. (A) 914 (1966)

126. J.Dyson and N.L.Paddock. Chem. Comm. 191 (1966)

127. F.A.Cotton, G.A.Rushholme and A.Shaver. J. Coord. Chem. 3 99 (1973)

128. [illegible].F.Ispert and [illegible]rivastava. J. Chem. Soc. (A) 210 (1966)

129. [illegible] Lote and [illegible].C.Harris. Chem. Comm. 407 (1972)

130. J.Trotter and S.H.Whitlow. J. Chem. Soc. (A) 455 (1970)

131. W.L.Nielsen. Inorg. Synth. 6 79 (1960)

132. A.F.Grapov, N.N.Mel'nikov and L.V.Razvodovskaya. Russ. Chem. Rev. 39 20 (1970)

133. H.G.Horn and M.Becke-Goehring. Z. anorg. Chem. 367 165 (1969)

134. O.J.Scherer and G.Schnabl. Z. Naturforsch. 31B 1462 (1976)

135. A.Michaelis and G.Schroeter. Chem. Ber. 27 490 (1894)

136. H.W.Grimmel, A.Guenther and J.F.Morgan. J. Amer. Chem. Soc. 68 539 (1946)

137. G.S.Harris. Proc. Chem. Soc. 118 (1957)

138. R.R.Holmes. J. Amer. Chem. Soc. 83 1334 (1960)

139. E.W.Abel and G.R.Willey. Proc. Chem. Soc. 308 (1962)

140. E.W.Abel, D.A.Armitage and G.R.Willey. J. Chem. Soc. 57 (1965)

141. R.R.Holmes and J.A.Forstner. Inorg. Chem. 2 380 (1963)

142. K.W.Muir and J.F.Nixon. Chem. Comm. 1405 (1971)

143. K.W.Muir. J. Chem. Soc. Dalton 259 (1975)

144. O.J.Scherer and P.Klusmann. Angew. Chem. Internat. Edn. 8 752 (1969)

145. R.Jefferson, J.F.Nixon and T.M.Painter. Chem. Comm. 622 (1969)

146. J.F.Nixon and B.Wilkins. Z. Naturforsch. 25B 649 (1970)

147. F.L.Bowden, A.T.Dronsfield, R.N.Haszeldine and D.R.Taylor. J. Chem. Soc. Perkin I 516 (1973)

148. G.Bulloch and R.Keat. J. Chem. Soc. Dalton 2010 (1974)

149. .Davies, .T.Dronsfield, .Hasseldine and D.P.Taylor. J. Chem. Soc. Perkin I 379 (1973)

150. R.Jefferson, J.F.Nixon, T.M.Painter,R.Keat and L.Stobbs. J. Chem. Soc. Dalton 1414 (1973)

151. O.J.Scherer and .Glassel. Angew. Chem. Internat. Edn. 14 629 (1975)

152. G.Bulloch and R.Keat. J. Chem. Soc. Dalton 1113 (1976)

153. E.Niecke, .Flick and S.Pohl. Angew. Chem. Internat. Edn. 15 309 (1976)

154. O.J.Scherer and G.Schnabl. Chem. Ber. 109 2996 (1976)

155. O.J.Scherer and G.Schnabl. Z. Naturforsch. 31B 1462 (1976)

156. O.J.Scherer and G.Schnabl. Angew. Chem. Internat. Edn. 15 772 (1976)

157. .Zeiss. Angew. Chem. Internat, Edn. 15 555 (1976)

158. G.Bulloch, R.Keat and D.G.Thompson. J. Chem. Soc. Dalton 99 (1977)

159. R.Keat and D.G.Thompson. Angew. Chem. Internat. Edn. 16 797 (1977)

160. G.Bulloch, R.Keat and D.G.Thompson. J. Chem. Soc.Dalton 99 (1977)

161. G.Bulloch, R.Keat and D.G.Thompson. J. Chem. Soc. Dalton 1044 (1977)

162. .Zeiss and J.Weis. . Naturforsch. 32B 485 (1977)

163. .Dalgeish, R.Keat, A.Porte and .Shaw. J. Chem. Soc. Dalton 1505 (1977)

164. R.Keat, .Keith, .Macphee, K. .Muir and .G.Thompson. Chem. Comm. 372 (1978)

165. S.Pulloch, R.Keat and D.Rycroft. J. Chem. Soc. Dalton 764 (1978)

166. W. Weiss, C.Feldt, J. eis and G.Dunkel. Chem. Ber. 1180 (1978)

167. R. eat and D.G.Thompson. J. Chem. Soc. Dalton 634 (1978)

168. . ess and . eiss . aturforsch. 33B 723 (1978)

169. M.L.Thompson, R.Curtis Haltiwanger and A.D.Norman. Chem. Comm. 647 (1979)

170. S.Pohl. Z. Naturforsch. 34B 256 (1979)

171. S.Goldschmidt and . .Krauss. Angew. Chem. 67 471 (1955)

172. . . .Ibrahim, . .Shaw, C.P.Thakur, G.J.Bullen, J.S.Rutherford, P.A.Tucker, T.S.Cameron, . .Howlett and C. .Prout. Phosphorus 1 153 (1971)

173. Lj. anojlovic- uir and . . uir. J. Chem. Soc. Dalton 2395 (1974)

174. M.B.Peterson and .J. agner. J. Chem. Soc. Dalton 106 (1973)

175. D.W.J.Cruickshank. Acta Cryst. 17 671 (1964)

176. A.J.Wagner and . os. Acta Cryst. 24B 1423 (1968)

177. L.C.Thomas and R.A.Chittenden. Chem. Ind. 1913 (1961)

178. J.Emsley and D.Hall. "The chemistry of phosphorus." Harper and ow (1976)

179. L.J.Bellamy. "The infra-red spectra of complex molecules." ethuen (1964)

180. . athis, L.Lafaille and R.Burgada. Spectrochim. Acta 30 357 (1974)

181. V.Gutman, . tvary and .Fermen. onatsh. 97 1745 (1966)

182. A.C.Chapman, .C. olmes, .L.Paddock an .Searle.
J. Chem. Soc. 1825 (1961)

183. A.D. estland and . estland. Canad. J. Chem. 43 426 (1965)

184. I.R.Beattie and R.Collis. J. Chem. Soc. (A) 2960 (1969)

185. F.Calderazzo, S.Losi and . . usz. Inorg. Chim. Acta 3 329 (1969)

186. G. .A.Fowles and . . alton. J. Chem. Soc 4330 (1964)

187. J.Chatt and R.Hayter. J. Chem. Soc. 1343 (1963)

188. G. .A.Fowles and R.A. alton. J. Less-Common Metals 5 510 (1963)

189. R.J.H.Clark, R.H. .Negrotti and R.S.Nyholm. Chem. Comm. 486 (1966)

190. .Zeiss and C.Feldt. J. Organometallic Chem. 127 C5 (1977)

191. J.Chatt and H. . atson. J. Chem. Soc. 4980 (1961)

192. S.O.Grim, J.del Gaudio, R.P.Molenda, C.A.Tolman and J.P.Jesson. J. Amer. Chem. Soc. 96 3416 (1974)

193. D.S.Payne and A.P. alker. J. Chem. Soc. (C) 498 (1966)

194. K.K.Cheung, T.F.Lai and K.S. ok. J. Chem. Soc. (A) 1644 (1971)

195. P.S.Braterman, D. .Milne, E. .Randall and .Rosenberg. J. Chem. Soc. Dalton 1027 (1973)

196. .Hieber and .Freyer. Chem. Ber. 93 462 (1960)

197. R.H.Reimann and .Singleton. J. Organometallic Chem. 38 113 (1972)

198. .Sacco. Gazzetta 93 698 (1963)

199. R.Colton and C.J.Commons. Austral. J. Chem. 28 1673 (1975)

200. For a review of this work see F.A.Cotton. Progr. Inorg. Chem. 21 1 (1976)

201. F.A.Cotton and J.M.Troup. J. Amer. Chem. Soc. 96 3438 (1974)

202. W.Heiber and H.Beutner. Angew. Chem. 74 154 (1962)

203. F.A.Cotton, J.R.Kolb and B.R.Stults. Inorg. Chim. Acta 15 239 (1975)

204. F.A.Cotton and J.M.Troup. J. Amer. Chem. Soc. 96 5070 (1974)

205. F.A.Cotton and J.M.Troup. J. Amer. Chem. Soc. 96 1233 (1974)

206. F.A.Cotton, M.I.Hardcastle and G.A.Rushulme. J. Coord. Chem. 2 217 (1973)

207. F.A.Cotton and J.M.Troup. J. Amer. Chem. Soc. 96 4422 (1974)

208. M.Heberhold and K.Leonhard. J. Organometallic Chem. 78 253 (1974)

209. F.A.Cotton, B.E.Hanson, J.D.Jamerson and B.R.Stults. J. Amer. Chem. Soc. 99 3293 (1977)

210. F.A.Cotton and P.Lahuerta. Inorg. Chem. 14 116 (1975)

211. P.A.Wegner, L.P.Evans and J.Haddock. Inorg. Chem. 14 192 (1975)

212. D.J.Thornhill and A.R.Manning. J. Chem. Soc. Dalton 2086 (1973)

213. J.P.Crow, W.R.Cullen, F.Harrison and J.Trotter. J. Amer. Chem. Soc. 92 6339 (1970)

214. J.P.Crow and W.R.Cullen. Inorg. Chem. 10 2165 (1971)

215. T.L.Peterson and [illegible].I.Watters. Inorg. Chem. 12 3009 (1973)

216. [illegible].Heiber and F.Kummer. Chem. Ber. 100 148 (1967)

217. A.R.Sanger. Chem. Comm. 893 (1975)

218. [illegible].T.[illegible]ague and J.P.[illegible]itchener. Inorg. Chem. 8 119 (1969)

219. [illegible].T.[illegible]ague. Inorg. Chem. 8 1975 (1969)

220. A.R.Sanger. J. Chem. Soc. Dalton 120 (1977)

221. [illegible].A.Bennett, [illegible].J.H.Clark and [illegible].L.[illegible]ilner. Inorg. Chem. 6 1647 (1967)

222. [illegible].Heiber and [illegible].[illegible]eutner. [illegible] Chem. Internat. Edn. 1 116 (1962)

223. [illegible].Heiber and H.Beutner. [illegible] anorg. Chem. 317 63 (1962)

224. [illegible].Heiber and [illegible].[illegible]erner. Chem. Ber. 90 286 (1957)

225. [illegible].Heiber and A.Lipp. Chem. Ber. 92 2075 (1959)

226. [illegible].Heiber and A.Lipp. Chem. Ber. 92 2085 (1959)

227. W.Heiber, [illegible].Beck and G.Braun. Angew. Chem. 72 795 (1960)

228. [illegible].Heiber. Adv. Organometallic Chem. 8 1 (1970)

229. T.A.Manuel. Adv. Organometallic Chem. 3 233 (1965)

230. F.Calderazzo, [illegible].Ercoli and G.Natta. in "Organic syntheses via metal carbonyls." Eds. I.[illegible]ender and P.Pino. Wiley-Interscience (1968)

231. [illegible].Heiber and J.G.Floss. Chem. Ber. 90 1617 (1957)

232. [illegible].Heiber and [illegible].[illegible]ahlen. Chem. Ber. 91 2223 (1958)

233. [illegible].F.[illegible]dgell, M.T.[illegible], [illegible].J.[illegible]ulkin, [illegible].[illegible]ayer and [illegible].[illegible]oizuri. J. Amer. Chem. Soc. 87 [illegible] (1965)

234. [illegible].[illegible]eiber, [illegible] and [illegible]. [illegible] 90 [illegible]78 (1957)

235. H.Kisch. J. Organometallic Chem. 38 219 (1972)

236. C.Kruger. Chem. Ber. 106 3230 (1973)

237. R.P.Bennett. Inorg. Chem. 9 2184 (1970)

238. M.Heberhold and W.Golla. J. Organometallic Chem. 26 C27 (1971)

239. R.G.Little and R.J.Doedens. Inorg. Chem. 11 1392 (1972)

240. A.Albini and H.Kisch. Angew. Chem. Internat. Edn. 14 182 (1975)

241. H.Alper. J. Organometallic Chem. 50 209 (1973)

242. A.Albini and H.Kisch. J. Organometallic Chem. 94 75 (1975)

243. M.Ciampolini and N.Nardi. Inorg. Chem. 5 1150 (1966)

244. M.Di Vaira and P.L.Orioli. Acta Cryst. B24 1269 (1968)

245. L.V.Interrante. Inorg. Chem. 7 943 (1968)

246. S.K.Madan, W.M.Reiff and J.C.Bailar. Inorg. Chem. 4 1366 (1965)

247. P.Paoletti, M.Ciampolini and L.Sacconi. J. Chem. Soc. 3589 (1963)

248. S.K.Madan and J.Peone. Inorg. Chem. 6 463 (1967)

249. J.Glerup, J.Josephsen, K.Michelsen, E.Pedersen and C.E.Schaffer. Acta Chem. Scand. 24 247 (1970)

250. D.M.Duggan and D.N.Hendrickson. Chem. Comm. 411 (1973)

251. S-T.Yuan, V.Miller and S.K.Madan. Inorg. Chim. Acta 7 134 (1973)

252. S.M.Nade and G.F.Gilley. Inorg. Nuclear Chem. Letters 14 363 (1978)

253. D.Marongiu, E.G.Lingafelter and P.Paoletti. Inorg. Chem. 8 2763 (1969)

254. D.A.Buckingham and D.Jones. Inorg. Chem. 4 1387 (1965)

255. S.C.Nyburg and J.S.Wood. Inorg. Chem. 3 468 (1964)

256. A.McPherson, M.G.Rosoman, D.W.Margerum and M.R.James. J. Coord. Chem. 1 39 (1971)

257. R.L.Wilder, D.A.Kamp and C.S.Garner. Inorg. Chem. 10 1393 (1971)

258. G.Schwarzenbach. Helv. Chim. Acta 36 23 (1953)

259. J.Hughes and G.R.Willey. J. Coord, Chem. 4 33 (1974)

260. J.Hughes and G.R.Willey. Inorg. Chim. Acta 13 L1 (1975

261. M.Ciampolini, A.Cristini, A.Diaž and G.Ponticelli. Inorg. Chim. Acta 7 549 (1973)

262. F.Basolo and R.G.Pearson "Mechanisms of inorganic reactions." 2nd. Edition, Wiley (1967)

263. F.Arenare, P.Paoletti, A.Dei and A.Vacca. J. Chem. Soc. Dalton. 736 (1972)

264. R.Barbucci, L.Fabbrizzi, P.Paoletti and A.Vacca. J. Chem. Soc. Dalton 740 (1972)

265. P.Paoletti, L.Fabbrizzi and R.Barbucci. Inorg. Chim. Acta Rev. 7 43 (1973)

266. P.Paoletti, L.Fabbrizzi and R.Barbucci. Inorg. Chem. 12 1861 (1973)

267. M.F.Baldwin. J. Chem. Soc. 4369 (1960)

268. H.H.Schmidtke and D.Garthoff. Inorg. Chim. Acta 2 357 (1968)

269. F.A.Cotton in "Modern coordination chemistry." Eds. J.Lewis and R.G.Wilkins. Interscience (1960)

270. K.W.Kuo and S.K.Madan. Inorg. Chem. 6 1580 (1960)

271. R.B.King, P.N.Kapoor and R.N.Kapoor. Inorg. Chem. 10 1841 (1971)

272. R.B.King, R.N.Kapoor, M.S.Saran and P.N.Kapoor. Inorg. Chem. 10 1851 (1971)

273. R.B.King and M.S.Saran. Inorg. Chem. 10 1861 (1971)

274. R.B.King and J.C,Cloyd. Inorg. Chem. 14 1550 (1975)

275. J.W.Rathke and E.L.Muetterties. J. Amer. Chem. Soc. 97 3272 (1975)

276. M.L.H.Green and D.J.Jones. Adv. Inorg. Chem. Radiochem. 7 115 (1965)

277. M.Aresta, P.Giannoccaro, M.Rossi and A.Sacco. Inorg. Chim. Acta 5 203 (1971)

278. G.Hata, H.Kondo and A.Miyake.J.Amer.Chem.Soc. 90 2278(1968)

279. H.F.Klein. Angew. Chem. Internat. Edn. 9 904 (1970)

280. V.L.Goedken, S.Peng, J.Molin-Norris and Y.Park. J. Amer. Chem. Soc. 98 8391 (1976)

281. H.Nigam, R.S.Nyholm and D.V.R.Rao. J. Chem. Soc. 1397 (1959)

282. W.Jetz and W.A.G.Graham. Inorg. Chem. 10 4 (1971)

283. W.M.McClellan and R.M.Benson. J. Amer. Chem. Soc. 88 5165 (1966)

284. F.G.Mann and H.R.Watson. J. Chem. Soc. 2772 (1958)

285. J.T.Braunholtz, E.A.V.Ebsworth, F.G.Mann and N.Sheppard. J. Chem. Soc. 2780 (1958)

286. R.A.Walton. Progr. Inorg. Chem. 16 1 (1972)

288. R.J.H.Clark. "The chemistry of titanium and vanadium." Elsevier (1968)

289. C.S.Garner and D.A.House. in "Transition metal chemistry."

Fd. ?.L.Carlin ?arcel Dekker Inc. 6 59 (1970)

289. J.C.Taft and M.M.Jones. J. Amer. Chem. Soc. 82 4196 (1960)

290. ?.J.Kern. J. Inorg. Nuclear Chem. 24 1105 (1962)

291. G.?.A.Fowles and R.A.Hoodless. J. Chem. Soc. 33 (1963)

292. ?.?.Duckworth, G.?.A.Fowles and R.A.Hoodless. J. Chem. Soc. 5665 (1963)

293. G.W.A.Fowles, T.E.Lester and B.J.Russ. J. Chem. Soc. (A) 805 (1968)

294. M.Antler and A.?.Laubengayer. J. Amer. Chem. 77 5250 (1955)

295. ?.?.Duckworth, G.?.A.Fowles and ?.?.Greene. J.Chem. Soc. (A) 1592 (1967)

296. B.J.Russ and J.S.Wood. Chem. Comm. 745 (1966)

297. G.W.A.Fowles, P.T.Greene and J.S.Wood. Chem.Comm. 971 (1967)

298. P.T.Greene and P.L.Orioli. J. Chem. Soc. (A) 1621 (1969)

299. G.W.A.Fowles and P.T.Greene. Chem. Comm. 784 (1966)

300. G.W.A.Fowles and P.T.Greene. J. Chem. Soc. (A) 1869 (1967)

301. G.?.A.Fowles and ?.A.Walton. J. Chem. Soc. 4953 (1964)

302. ?.C.Alyea, D.C.Bradley and R.G.Copperthwaite. J. Chem. Soc. Dalton. 1580 (1972)

303. J.Hughes and G.R.Willey. Inorg. Chim. Acta 13 L1 (1975)

304. J.Hughes and G.R.Willey Inorg. Chim. Acta 12 143 (1975)

305. J.Hughes and G.R.Willey. Inorg. Chim. Acta 24 L1 (1977)

306. H.Yada, J.Tanaka and S.Nagakura. J. Mol. Spectroscopy 9 461 (1962)

307. R.Kiesel and E.P.Schram. Inorg. Chem. 12 1090 (1973)

308. J.Hughes and G.R.Willey. Inorg. Chim. Acta 20 137 (1976)

309. G.R.Willey. Inorg. Chim. Acta 21 L12 (1977)

310. P.C.Crouch, G.W.A.Fowles and R.A.Walton. J. Chem. Soc. (A) 972 (1969)

311. G.W.A.Fowles and T.E.Lester. Chem. Comm. 47 (1967)

312. G.W.A.Fowles, T.E.Lester and R.A.Walton. J. Chem. Soc. 1081 (1968)

313. D.G.Holah and J.P.Fackler. Inorg. Chem. 5 479 (1966)

314. D.G.Holah and J.P.Fackler. Inorg. Chem. 4 1112 (1965)

315. J.F.Earley and R.D.Cannon. in "Transition metal chemistry." Ed. R.L.Carlin. 1 33 (1965)

316. F.A.Cotton and G.Wilkinson. "Advanced inorganic chemistry." 3rd. Edition. Interscience 679 (1972)

317. M. Pierce-Butler and G.R.Willey. J. Organometallic Chem. 54 C19 (1973)

318. N.W.Alcock, M.Pierce-Butler and G.R.Willey. Chem. Comm. 627 (1974)

319. N.W.Alcock, M.Pierce-Butler and G.R.Willey. J. Chem. Soc. Dalton 707 (1976)

320. A.C.Skapski, P.G.Troughton and H.H.Sutherland. Chem. Comm. 1418 (1968)

321. A.C.Skapski and P.G.Troughton. Acta Cryst. B26 716 (1970)

322. R.D.Gorsich. J. Amer. Chem. Soc. 82 4211 (1960)

323. R.S.P.Coutts, R.L.Martin and P.C.Wailes. Inorg. Nuclear Chem. letters 9 49 (1973)

324. D.C.Bradley and E.G.Torrible. Canad. J. Chem. 41 134 (1963)

325. A.Feltz. Z. Chem. 3 274 (1963)

326. A.Feltz. Z. anorg. Chem. 332 35 (1964)

327. A.Feltz. Z. anorg. Chem. 338 155 (1965)

328. H.Kopf, B.Block and M.Schmidt. Chem. Ber. 101 272 (1968)

329. E.G.Muller, J.L.Petersen and L.F.Dahl. J. Organometallic Chem. 111 91 (1976)

330. E.F.Epstein, I.Bernal and H.Kopf. J. Organometallic Chem. 26 229 (1971)

331. H.Kopf. Chem. Ber. 102 1509 (1969)

332. P.E.Jones and L.Katz. Chem. Comm. 842 (1967)

333. H.Kopf. Angew. Chem. Internat. Edn. 8 375 (1969)

334. B.R.Davies and I.Bernal. J. Mol. Structure 2 135 (1972)

335. B.Csakvari, Zs.Wagner, P.Gomory, F.C.Mijlhoff, B.Rozsondai and I.Hargittai. J. Organometallic Chem. 107 287 (1976)

336. C.Glidewell and D.C.Liles. Chem. Comm. 632 (1977)

337. H.Puff, E.Gattermeyer, R.Hundt and R.Zimmer. Angew. Chem. Internat. Edn. 16 547 (1977)

338. D.W.Cruickshank. J. Chem. Soc. 5486 (1961)

339. L.H.Sommer. "Stereochemistry, mechanism and silicon." McGraw-Hill (1965)

340. C.Eaborn. "Organosilicon compounds." Butterworths (1960)

341. H.Kriegsman. Z. Elektrochem. 61 1088 (1957)

342. E.W.Abel and D.A.Armitage. Adv. Organometallic Chem. 14 285 (1968)

343. E.W.Abel, D.A.Armitage and R.P.Bush. J. Chem. Soc. 2455 (1964)

344. E.W.Abel and C.R.Jenkins. J. Organometallic Chem. 14 285 (1968)

345. P.H.Boorman, T.Chivers, K.N.Mahadev and B.D.O'Dell. Inorg. Chim. Acta 19 L35 (1976)

346. D.C.Bradley. Coordination Chem. Rev. 2 299 (1967)

347. M.G.Voronkov, V.P.Mileshekevich and Yu.A.Yuzhelevskii. Russ. Chem. Rev. 45 1167 (1976)

348. K.A.Andrianov. "Metal Organic Polymers." Wiley-Interscience (1965)

349. E.A.V.Ebsworth. "Volatile silicon compounds." Pergamon (1963)

350. J.D.Danforth. J. Amer. Chem. Soc. 80 2585 (1958)

351. B.N.Dolgov, N.F.Orlov and M.G.Voronkov. Izvest. Akad. Nauk. SSSR. Otdel. Khim. Nauk. 1408 (1959) Chem. Abs. 54 1271i (1960)

352. A.L.Suvorov and S.S.Spaskii. Uspekhi. Khim. 28 1267 (1959)

353. V.V.Yastrebov. Russ. J. Phys. Chem. 46 1064 (1972)

354. C.G.Barraclough, D.C.Bradley, J.Lewis and I.M.Thomas. J. Chem. Soc. 2601 (1961)

355. G.S.Kyker and E.P.Schram. Inorg. Chem. 8 2313 (1969)

356. T.A.Zeitler and C.A.Brown. J. Phys. Chem. 61 1174 (1957)

357. H.Suzuki and T.Takiuchi. Bull. Chem. Soc. Japan.

48 2460 (1975)

358. W.S.Tatlock and E.G.Rochow. J. Org. Chem. 17 1555 (1952)

359. N.Wright and M.J.Hunter. J. Amer. Chem. Soc. 69 803 (1947)

360. C.W.Young, P.C.Servais, C.C.Currie and M.J.Hunter. J. Amer. Chem. Soc. 70 3758 (1948)

361. A.L.Smith. Spectrochim. Acta 16 87 (1960)

362. G.W.A.Fowles, D.F.Lewis and R.A.Walton. J. Chem. Soc. (A) 1468 (1968)

363. R.A.Walton. Progr. Inorg. Chem. 16 103 (1972)

364. K.L.Baker, D.A.Edwards, G.W.A.Fowles and R.G.Williams. J. Inorg. Nuclear Chem. 29 1881 (1967)

365. J.C.Drake, J.Vekris and J.S.Wood. J. Chem. Soc. (A) 1000 (1968)

366. S.A.Giddings. Inorg. Chem. 3 684 (1964)

367. J.S.Skelsey. Diss. Abs. 22 4177 (1962)

368. J.G.Noltes and G.J.M.Van der Kerk. Rec. Trav. chim. 81 39 (1962)

369. R.A.Walton. Quart. Rev. 19 12[illegible] (1965)

370. W.V.Graven and W.V.Petersen. J. Inorg. Nuclear Chem. 31 1743 (1969)

371. D.C.Bradley and I.M.Thomas. J. Chem. Soc. 3404 (1959)

372. D.C.Bradley, R.N.Kapoor and B.C.Smith. J. Chem. Soc. 204 (1963)

373. V.V.Yastrebov and A.I.Chernyshev. J. Gen. Chem. (USSR) 37 2032 (1967)

374. R.A.Rice. Coordination Chem. Rev. [illegible] 199 (19[illegible])

375. P.Ehrlich and [illegible].Siebert. Z. anorg. Chem. 301 288 (1959)

376. T. Harada. Bull. Chem. Soc. Japan 17 281 (1942)

377. H.Kriegsman and H.Hoffmann. Z. Chem. 3 268 (1963)

378. D.Seyferth. J. Amer. Chem. Soc. 79 5881 (1957)

379. E.J.Kupchick and P.J.Calabretta. Inorg. Cehm. 4 973 (1965)

380. H.Kriegsman, H.Hoffmann and H.Geissler. Z. anorg. Chem. 359 58 (1968)

381. M.B.Robin and P.Day. Adv. Inorg. Chem. Radiochem. 10 247 (1967)

382. G.C.Allen and N.S.Hush. Progr. Inorg. Chem. 8 357 (1967)

383. N.S.Hush. Progr. Inorg. Chem. 8 391 (1967)

384. D.O.Cowan, C.LeVanda, J.Park and F.Kaufman. Accounts Chem. Res. 6 1 (1973)

385. W.H.Morrison and D.N.Hendrickson. Inorg. Chem. 14 2331 (1975)

386. R.R.Gagne, C.A.Koval and T.J.Smith. J. Amer. Chem. Soc. 99 8367 (1977)

387. J.C.Smart and B.L.Pinsky. J. Amer. Chem. Soc. 99 956 (1977)

388. Y.Jeannin, J-P.Launay, J.Livage and A.Nel. Inorg. Chem. 17 374 (1978)

389. T.J.Meyer. Accounts Chem. Res. 11 94 (1978)

390. R.D.Cannon. Adv. Inorg. Chem. Radiochem. 21 179 (1978)

391. J.E.Sutton, P.M.Sutton and H.Taube. Inorg. Chem. 18 1017 (1979)

392. A.Yeh, A.Haim, M.Tanner and A.Ludi. Inorg. Chim. Acta 33 51 (1979)

393. Ya.G.Goroschenko and M.M.Godneva. Russ. J. Inorg. Chem. 6 744 (1961)

394. C.K.Jorgensen. Acta Chem. Scand. 11 73 (1957)

395. P.G.Bennett and D.Nicholls. J. Chem. Soc. (A) 1204 (1971)

396. R.L.King and J.A.Neptune. J. Amer. Chem. Soc. 77 3186 (1955)

397. E. .Abel and D.A.Armitage. Adv. Organometallic Chem. 5 1 (1967)

398. H.Schumann, O.Stelzer and W.Grick. Angew. Chem. Internat. Edn. 8 271 (1969)

399. H.Kopf and K.H.Rathlein. Angew. Chem. Internat. Edn. 8 980 (1969)

400. A.R.Dias and M.L.H.Green. Chem. Comm. 962 (1969)

401. K.K.Joshi, R.Harole and V.A.Wilson. Inorg. Nuclear Chem. Letters 6 49 (1970)

402. P.S.Braterman, V.A.Wilson and K.K.Joshi. J. Chem. Soc. (A) 191 (1971)

403. T.S.Cameron, C.K.Prout, G.V.Rees, M.L.H.Green, K.K.Joshi, G.R.Davies, B.T.Kilbourn, P.S.Braterman and V.A.Wilson. Chem. Comm. 14 (1971)

404. A.R.Dias and M.L.H.Green. J. Chem. Soc. (A) 1951 (1971)

405. W.E.Douglas, M.L.H.Green. C. .Prout and G.V.Rees. Chem. Comm. 896 (1971)

406. P.S.Braterman, V.A.Wilson and K.K.Joshi. J. Organometallic Chem. 31 123 (1971)

407. P.S.Braterman and V.A.Wilson. J. Organometallic Chem. 31 131 (1971)

408. A.R.Diss and M.L.H.Green. J. Chem. Soc. (A) 2807 (1971)

409. F.Sato, T.Uemura and M.Sato. J. Organometallic Chem. 56 C27 (1973)

410. R.Zanella, R.Ross and M.Graziani. Inorg. Chem. 12 2736 (1973)

411. M.Sato and T.Yoshida. J. Organometallic Chem. 94 403 (1975)

412. G.R.Davies and B.T.Kilbourn. J.Chem. Soc. (A) 87 (1971)

413. T.A.Brown, A.K.Glass and B.Kumar. J. Chem. Soc. (A) 1510 (1969)

414. D.C.Bradley and P.A.Hammersley. J. Chem. Soc. (A) 1894 (1967)

415. M.Schmidt, H-J.Dersin and H.Schumann. Chem. Ber. 95 1428 (1962)

416. G.Fachinetti and C.Floriani. J. Chem. Soc. Dalton 2433 (1974)

417. M.G.Harris, M.L.H.Green and W.E.Lindell. J. Chem. Soc. (A) 1453 (1969)

418. L.F.Lindoy. Coordination Chem. Rev. 4 41 (1969)

419. E.W.Abel, B.C.Crosse and D.B.Brady. J. Amer. Chem. Soc. 87 4397 (1965)

420. P.Woodward, L.F.Dahl, E.W.Abel and B.C.Crosse. J. Amer. Chem. Soc. 87 5251 (1965)

421. E.W.Abel, D.B.Brady and B.C.Crosse. J. Organometallic Chem. 5 260 (1966)

422. E.W.Abel and B.C.Crosse. J. Chem. Soc. (A) 1141 (1966)

423. [illegible] Abel and [illegible] Crosse. J. Chem. Soc. (A) 1377 [illegible]
424. [illegible] Abel, [illegible] Atkins, B.C.Crosse and G.V.Hutson. J. Chem. Soc. (A) 687 (1968)
425. S.Kuzuka and S.Ohya. J. Organometallic Chem. 149 161 (1978)
426. P.C.Bharara. J. Organometallic Chem. 121 199 (1976)
427. A.N.Nesmeyanov, G.V.Nogina, A.M.Berlin, A.S.Gershovich and G.V.Shatalov. Izvest. Akad. Nauk. SSSR. 2146 (1961): Chem. Abs. 57 11[illegible]1f (196[illegible])
428. [illegible] J. Chem. Soc. Dalton 1891 (1975)
429. Trivalent antimony, either intramuscular or intravenous and lucanthone hydrochloride by mouth, have been the only drugs available for many years for the treatment of schistosomiasis. Schistosomiasis is a disease in which humans are parasitized by blood flukes, the adult worms inhabit the blood vessels. Also known as bilharziasis it is found in Africa, South America, India, Asia and the near East.
430. A severe, generalised and often fatal infection caused by parasites of the genus Leishmania, which are carried by sand flies. Antimony compounds and the aromatic diamidines produce a cure. Endemic in Central and North Africa, India and China.
431. G.Booth. Adv. Inorg. Chem. Radiochem. 6 1 (1964)
432. D.H.Boal and G.A.Ozin. J. Chem. Soc. Dalton 1824 (1973)
433. R.Okawara and Y.Matsumura. Adv. Organometallic Chem. 14 187 (1976)
434. [illegible] J. Amer.Chem.Soc. 75 [illegible] (1954)

435. J.[illegible].Smith in "Comprehensive Inorganic Chemistry" Eds J.C.Bailar, H.J.Emeleus, R.S.Nyholm and A.F.Trotman- Dickinson, Pergamon Press 2 641 (1973).

436. L.Kolditz in "Halogen Chemistry" Ed V.Gutman Academic Press 2 153 (1967).

437. F.Hulme and J.C.Scruton. J. Chem. Soc. (A) 2448 (1968)

438. I.Lindquist. "Inorganic Adduct Molecules of Oxo-Compounds" Springer, Berlin (1963).

439. J.W.Cameron and R.C.G.Killean. Cryst. Struct. Comm. 1 31 (1972).

440. S.K.Porter and R.A.Jacobson. J. Chem. Soc. (A) 1356 (1970).

441. S.K.Porter and R.A.Jacobson. J. Chem. Soc. (A) 1359 (1970)

442. B.K.Roberts, W.G.McPherson and E.A.Meyers. J. Phys. Chem. 71 3531 (1967)

443. W.G.McPherson and E.A.Meyers. J. Phys. Chem. 72 3117 (1968)

444. A.M.Brodie and C.J.Wilkins. Inorg. Chem. Acta 8 13 (1974)

445. M.R.Truter. Acta Cryst. 22 556 (1967)

446. M.M.Elcombe and J.C.Taylor. Acta Cryst. 24A 410 (1968)

447. J.Stewart. J. Chem. Phys. 26 248 (1957)

448. G.[illegible].Lin and H.Hope. Acta Cryst. 28B 623 (1972)

449. O.Foss, J.Johnsen and O.Tredten. Acta. Chem. Scand. 12 1782 (1958)

450. E.F.Reid. "Organic Chemistry of Bivalent Sulphur" Vol V, Chemical Publishing Co. (1963)

451. T.J.Lane, A.Yamaguchi, J.V.Quagliano, J.A.Ryan and S.Mizushima. J. Amer. Chem. Soc. 81 3824 (1959)

452. P.P.Singh and I.M.Pande. J. Inorg. Nuclear Chem. 34 591 (1972)

453. M.M.Khan. J. Inorg. Nuclear Chem. 37 162[illegible] (1975)

454. R.K.Gosavi, U.Agarwala and C.N.R.Rao. J. Amer. Chem. Soc. 89 235 (1967)

455. A.C.Hiremath and A.S.R.Murty. Current. Sci. 45 545 (1976)

456. M.B.Adi and A.S.R.Murty. J. Inorg. Nuclear Chem. 39 692 (1977)

457. A.Yamaguchi, R.B.Penland, S.Mizushima, T.J.Lane, C.Curran and J.V.Quagliano. J. Amer. Chem. Soc. 80 527 (1958)

458. G.D.Saralidze, A.K.Molodkin and U.C.Omuralieva, Russ. J. Inorg. Chem. 17 1[illegible]51 (1972)

459. R.K.Gosavi and C.N.R.Rao. J. Inorg. Nuclear Chem. 29 1937 (1967)

460. M.H.Sonar and A.S.R.Murty. J. Inorg. Nuclear Chem. 39 2155 (1977)

461. T.N.Srivastava, P.C.Srivastava and B.Bajpai. J. Inorg. Nuclear Chem. 40 922 (1978)

462. P.Askalani and R.A.Bailey. Canad. J. Chem. 47 2275 (1969)

463. E.Cervone, P.Cancellieri and C.Furlani. J. Inorg. Nuclear Chem. 30 2431 (1968)

464. S.L.Holt and R.L.Carlin. J. Amer. Chem. Soc. 86 3017 (1964)

465. R.Rivest. Canad. J. Chem. 40 2234 (1962)

466. D.S.Bystrov, T.N.Sumarokova and V.N.Filiminov. Optics and Spectroscopy. 9 239 (1960)

467. S.E.Livingstone. Quart. Rev. 19 406 (1965)

468. L.G.Sillen and A.E.Martell "Stability Constants of Metal-ion complexes" Chem. Soc. Special Publ. No.17 (1964)

469. M.Nardelli. Gazzetta 89 1616 (1959)

470. M.Nardelli, A.Braibanti and G.Fava. Gazzetta 87 1209 (1957)

471. L.Cavalca, M.Nardelli and A.Braibanti. Grazzetta 86 942 (1956)

472. K.Jensen and P.H.Nielsen. Acta. Chem. Scand. 20 597 (1966)

473. C.Collard-Charon and M.Renson. Bull. Soc. chim. Belges. 72 149 (1963)

474. L.P.Battaglia, A.Bonamartini Corradi, G.Pelizzi, and M.E.Vidoni Tani. Cryst. Struct. Comm. 4 399 (1975)

475. L.P.Battaglia, A.Bonamartini Corradi, G.Pelizzi and M.E.Vidoni Tani. J. Chem. Soc. Dalton. 1141 (1977)

476. K.J.Wynne. J. Chem. Educ. 50 328 (1973)

477. V.B.Anand and B.R.Prasad. Z. anorg. Chem. 301 311 (1959)

478. F.D.Kellog and N.A.Nistaivoff. Inorg. Nuclear Chem. Letters. 4 47 (1968)

479. R.H.Sahasrabudhey and H.Krall. J. Indian Chem. Soc. 21 63 (1944)

480. R.H.Sahasrabudhey and H.Krall. J. Indian Chem. Soc. 22 37 (1945)

481. G.Walter. Ber. Dtsch. Chem. Ges. B. 64 1087 (1931)

482. R.T.C. Loh and W.M.Dehn. J. Amer. Chem. Soc. 48 2956 (1926)

483. P.H.Javora, E.A.Meyers and R.A.Zingaro. Inorg. Chem. 15 2525 (1976)

484. D.J.Williams, G.M.Newton and K.J.Wynne. Cryst. Struct. Comm. 6 167 (1977)

485. D.J.Williams and K.J.Wynne. Inorg. Chem. 17 1108 (1978)

486. W.R.Trost. Canad. J. Chem. 32 356 (1954)

487. R.R.Holmes and E.F.Bertaut. J. Amer. Chem. Soc. 80 2980 (1958)

488. R.R.Holmes and E.F.Bertaut. J. Amer. Chem. Soc. 80 2983 (1958)

489. R.R.Holmes. J. Phys. Chem. 64 1295 (1960)

490. R.R.Holmes. J. Amer. Chem. Soc. 82 5285 (1960)

491. V.Mark, C.H.Dungan, M.M.Crutchfield and J.R.Van Wazer. Topics in Phosp. Chem. 5 227 (1967)

492. M.A.J.Jungsmen and C.Curran. Nature. 202 280 (1964)

493. J.R.VanWazer. "Phosphorus and its compounds" Interscience (1958)

494. H.Kopf and M.Schmidt. Z. anorg. Chem. 340 139 (1965)

495. M and T Chemicals Inc. Chem. Abs. 64 9766 (1966)

496. J.A.McCleverty and G. ilkinson. Inorg. Synth. 8 211 (1966)

497. R.O.Sauer. J. Amer. Chem. Soc. 66 1707 (1944)

498. D.A.Armitage, M.J.Clark, A.W.Sinden, J.N.Wingfield, E.W.Abel and E.J.Louis. Inorg. Synth. 15 207 (1974)

499. M.A.Bennett, L.Pratt, G.Wilkinson, J. Chem. Soc. 2037 (1961)

500. I.U.P.A.C. "Nomenclature of Inorganic Chemistry" Butterworths (1971)

501. J.C.T.R. Burckett St. Laurent, H.E.Hosseini, J.Sinclair and J.F.Nixon. Inorg. Chem. Acta. 44 L17 (1980)